Universidade Estadual de Campinas
Faculdade de Odontologia de Piracicaba

CÉSAR AUGUSTO GALVÃO ARRAIS

Cirurgião-Dentista

INFLUÊNCIA DOS MODOS DE ATIVAÇÃO NO GRAU DE CONVERSÃO, RESISTÊNCIA E MORFOLOGIA DA INTERFACE DE UNIÃO DE SISTEMAS DE CIMENTAÇÃO E ADESIVOS

Tese apresentada à Faculdade de Odontologia de Piracicaba - UNICAMP, como parte dos requisitos para obtenção do título de Doutor em Clínica Odontológica, Área de Dentística.

Orientador: Prof. Dr. Marcelo Giannini

PIRACICABA
-2006-

FICHA CATALOGRÁFICA ELABORADA PELA

BIBLIOTECA DA FACULDADE DE ODONTOLOGIA DE PIRACICABA
Bibliotecário: Marilene Girello – CRB-8ª. / 6159

Ar69i

Arrais, César Augusto Galvão.

Influência de diferentes modos de ativação no grau de conversão, resistência e morfologia de interface de união de sistemas de cimentação de dupla ativação utilizados em restaurações indiretas em compósito e de agentes de união. / César Augusto Galvão Arrais. -- Piracicaba, SP: [s.n.], 2006.

Orientadores: Marcelo Giannini, Frederick Allen Rueggeberg.

Tese (Doutorado) – Universidade Estadual de Campinas, Faculdade de Odontologia de Piracicaba.

1. Adesivos dentinários. 2. Cimentos de resina. 3. Polimerização. 4. Resistência dos materiais. 5. Dentina. I. Giannini, Marcelo. II. Rueggeberg, Frederick Allen. III. Universidade Estadual de Campinas. Faculdade de Odontologia de Piracicaba. IV. Título.

(mg/fop)

Título em inglês: Effect of different activation modes on the degree of conversion, tensile bond strength and interfacial morphology of dual-cured cementing systems used in indirect composite restorations
Palavras-chave em inglês (*Keywords*): 1. Dentin-bonding agents. 2. Resin cements. 3. Polymerization. 4. Tensile strength. 5. Dentin
Área de concentração: Dentística
Titulação: Doutor em Clínica Odontológica
Banca examinadora: Sillas Luiz Lordelo Duarte Junior; Roberto Ruggiero Braga; Carlos de Paula Eduardo; Guilherme Elias Pessanha Henriques, Marcelo Giannini
Data da defesa: 14/12/2006
Programa de Pós-Graduação: Clínica Odontológica

UNICAMP

UNIVERSIDADE ESTADUAL DE CAMPINAS
FACULDADE DE ODONTOLOGIA DE PIRACICABA

MENTE · MANV · CORDE

A Comissão Julgadora dos trabalhos de Defesa de Tese de DOUTORADO, em sessão pública realizada em 14 de Dezembro de 2006, considerou o candidato CESAR AUGUSTO GALVÃO ARRAIS aprovado.

PROF. DR. MARCELO GIANNINI

PROF. DR. SILLAS LUIZ LORDELO DUARTE JÚNIOR

PROF. DR. ROBERTO RUGGIERO BRAGA

PROF. DR. CARLOS DE PAULA EDUARDO

PROF. DR. GUILHERME ELIAS PESSANHA HENRIQUES

Dedico este trabalho,

a Deus,

por estar sempre presente em minha vida e na vida das pessoas que amo, me ajudando a superar os momentos difíceis.

aos meus pais, companheiros e amigos, **Telmo e Márcia**, pela participação e cumplicidade em cada passo que tenho dado. Não existo sem vocês...

aos meus irmãos **Cristiane** e **Marcos**, por não serem simplesmente irmãos, mas parte de minha existência e me trazerem inspiração para continuar caminhando...

AGRADECIMENTOS ESPECIAIS / SPECIAL ACKNOWLEDGMENTS

Ao Prof. Dr. Marcelo Giannini, que se tornou não só um orientador para os assuntos profissionais e pessoais, mas também passou a ser um verdadeiro amigo que a todo instante me ajudou a ultrapassar todos os obstáculos. Sua constante participação em todo este trajeto foi um grande diferencial no meu amadurecimento profissional e pessoal. Por tudo isto, meus mais sinceros agradecimentos e a expectativa de que o fim de um ciclo não signifique o fim de uma amizade;

To Dr. Frederick Rueggeberg, for allowing me to work at his lab, for never making me feel that something could be missing while I was there, for helping me all the time accomplish all tasks, for the uncountable and frequent talks we had many times, and for being the good friend that was always around.

To Sallie Rueggeberg, who made me feel comfortable at her home since the first day that I was there, for treating me like a son, for being present in all moments that I needed, for all attention and care to provide the best not only to me but also to my family when they were there, and for making me feel like I was living at my own home by including me in her family during all special moments they had together.

À Vanessa, minha amada e companheira, por toda paciência, tolerância, efetiva participação em tudo que fiz e tudo o que faço, e por jamais ter hesitado em me ajudar e estar ao meu lado em todos os instantes. Minha vida é hoje mais completa graças à sua luz.

AGRADECIMENTOS / ACKNOWLEDGMENTS

À Universidade Estadual de Campinas, nas pessoas do Magnífico Reitor Prof. Dr. José Tadeu Jorge e vice-reitor Prof. Dr. Fernando Ferreira Costa;

À Faculdade de Odontologia de Piracicaba, da Universidade Estadual de Campinas, nas pessoas do Prof. Dr. Thales Rocha de Matos Filho e do diretor associado Prof. Dr. Mário Fernando de Góes durante os anos 2005 e meados de 2006, e nas pessoas do Prof. Dr. Francisco Haiter Neto e do diretor associado Prof. Dr. Marcelo de Castro Meneghim desde então;

To the Medical College of Georgia (MCG), for allowing me work at some facilities and for providing me all benefits as a foreigner student;

Ao Prof. Dr. Mário Alexandre Coelho Sinhoreti, coordenador geral dos cursos de Pós-Graduação, ao Prof. Dr. Roger William Fernandes Moreira, coordenador do curso de Pós-Graduação em Clínica Odontológica durante os anos de 2004 e 2005 e à Prof. Dra. Renata Cunha Matheus Rodrigues Garcia, atual coordenadora do curso de Pós-Graduação em Clínica Odontológica;

À Fundação de Amparo à Pesquisa do Estado de São Paulo (FAPESP), pela concessão e prorrogação da bolsa de doutorado;

À Coordenação de Aperfeiçoamento de Pessoal de Nível Superior (CAPES), pela concessão da Bolsa PDEE (Programa de Doutorado no País com Estágio no Exterior);

Ao Prof. Dr. Elliot Watanabe Kitajima, do NAP/MEPA – ESALQ/USP, por facilitar o acesso às instalações do laboratório de Microscopia Eletrônica, e por todos os conhecimentos transmitidos;

Aos Professores da área de Dentística, Prof. Dr. José Roberto Lovadino, Prof. Dr. Luís Roberto M. Martins, Prof. Dr. Luís Alexandre M. S. Paulillo, Prof. Dr. Luiz André F. Pimenta e Prof. Dr. Gisele M. Marchi, por compartilharem o conhecimento com seus alunos;

To the professors from the Department of Oral rehabilitation, Dr. Daniel Chan, Dr. Kevin Frazier, Dr. Gary Holmes, Dr. Willian and Dr. Martha Brackett, for giving all support that I needed and for including me as part of their community;

To Dr. David Pashley, for all attention and suggestions, and for allowing me to work in his lab;

Aos "agregados" (cunhados) Marcos Arduca, por acompanhar de perto cada passo que dou e tornar os caminhos mais claros e mais simples para mim, e Lucila, pelo interesse e participação em cada etapa de minha vida;

Aos antigos e novos companheiros e amigos de Pós-Graduação, Vanessa Cavalli, Grace Dias de Souza, Vanessa Arias, Mirela Shinohara, Ricardo Sigemori, Denise Caselli, Celso Pedrosa Filho, Carol Erhardt, Fábio Mitsui, Alessandra Peris, Érica Teixeira, Celso, Marcelo Oliveira, Andréa Cavalcanti, pelo companheirismo e apoio em todos os momentos.

Aos mais novos colegas da Pós-Graduação Claudia Batitucci dos Santos Daroz, Cristiane Franco Pinto, Thiago Assunção Valentino, Maria Cecília Caldas Giorgi Tolosa, Débora Alves Nunes Leite Lima, Murilo de Souza Menezes, Paulo Vinícius Soares, Rodrigo Sversut, Maria Malerba Humel e Marina Di Francescantonio, pela convivência agradável e ajuda;

Aos meus amigos de república João Batista César Neto, Flávio Baggio Aguiar, André Figueiredo Reis, Alex José dos Santos, Bruno César Vasconcelos Gurgel, André Luis Faria e Silva, Paulo Simamoto Junior, Bernardo Brasileiro, Ricardo Alves de Souza e Rhonan Ferreira da Silva, pela convivência, companheirismo e por se tornarem verdadeiros irmãos em inúmeros momentos;

A Mara, que me adotou como um filho entre tantos outros “filhos” que ela tem cuidado durante todos estes anos.

Aos meus amigos Cecília Turssi e Anderson Hara, pelo exemplo de seriedade e por transmitirem sua experiência e conhecimento nos momentos em que mais precisei.

To my friends from the Department of Oral Rehabilitation the MCG, Jennifer, Cindy, Linda and Don, for being good friends and always help me do whatever I needed to do, and for making me feel as part of their “gang”.

A todos os co-autores dos artigos componentes deste trabalho de tese;

Às empresas 3M ESPE, Dentsply/Caulk, Bisco, Pentron e Kerr, pela doação dos materiais;

A todos que direta ou indiretamente contribuíram para a realização deste trabalho;

“Tempo virá em que pesquisa diligente e contínua esclarecerá aspectos que agora permanecem escondidos...Tempo virá em que os nossos descendentes ficarão admirados de que não soubéssemos particularidades tão óbvias a eles... Muitas descobertas estão reservadas para os que virão, quando a lembrança de nós estiver apagada. O nosso universo será um assunto sem importância, a menos que haja uma coisa a ser investigada a cada geração... A natureza não revela seus mistérios de uma só vez".

Sêneca, *Problemas Naturais* Livro 7, Século I.

RESUMO

A não fotoativação do sistema adesivo previamente à aplicação do cimento resinoso tem sido proposta quando sistemas de cimentação de dupla ativação (SCDA - sistemas adesivos de dupla ativação / cimentos resinosos de dupla ativação) são utilizados. Entretanto, existe uma carência de relatos científicos a respeito da efetividade dos SCDA. Os objetivos deste estudo foram: 1- avaliar a resistência de união (RU) e a morfologia da interface de união de restaurações indiretas de compósito através da utilização da microscopia confocal laser quando os sistemas adesivos de dupla ativação foram ou não fotoativados previamente à aplicação dos cimentos resinosos; 2- analisar o grau de conversão (GC), através da Espectroscopia Infravermelha Transformada de Fourier (FTIR), e a RU de SCDAs quando a fotoativação não foi realizada ou atenuada pela presença da restauração indireta; 3- avaliar o GC e resistência coesiva de sistemas de união quando utilizados diferentes unidades de fotoativação (LEDs e de luz halógena). A RU e resistência coesiva foram avaliadas através do ensaio de microtração. Para a análise em microscopia confocal laser, diferentes corantes foram incorporados nos SCDAs previamente à sua aplicação. Para a análise do GC, os SCDAs foram aplicados na superfície do diamante da unidade de reflectância total atenuada acoplada ao espectrômetro infravermelho. O GC dos sistemas de união não relacionados aos SCDAs foi obtido utilizando-se filmes de resina adesiva. Os resultados demonstraram que a não fotoativação do sistema adesivo de dupla ativação previamente à cimentação não afetou a RU, e que os valores foram até superiores para um SCDA de 4ª geração quando o agente de união não foi fotoativado. A análise em microscopia confocal laser exibiu variação nas características morfológicas da interface de união, variando de acordo com o SCDA utilizado e com o modo de ativação de ambos componentes (sistema adesivo e cimento resinoso). Para alguns SCDAs, o GC foi reduzido pela presença do disco de compósito posicionado entre o SCDA e a ponta da unidade fotoativadora. A não fotoativação dos SCDAs resultou em GC inferiores aos obtidos com exposição direta da luz. A não fotoativação da maioria dos SCDAs também resultou em valores inferiores de RU, exceto quando um sistema de 4ª geração foi utilizado. A utilização de LED resultou em GC inferior ao obtido quando a luz halógena foi utilizada mas não afetou a resistência coesiva dos sistemas adesivos avaliados. Pode-se concluir que a não fotoativação dos sistemas adesivos é uma alternativa aceitável durante a cimentação de restaurações indiretas, porém os SCDAs necessitam de luz fotoativadora para garantir adequada RU. A utilização de LEDs pode comprometer o GC dos sistemas adesivos.

Palavras-chave: Adesivos dentinários, Cimentos de resina, Polimerização, Resistência à tração, Dentina,.

ABSTRACT

The lack of light-activation of dual-cured bonding agents before the resin cement application has been an alternative technique of cementing indirect restorations when dual-cured cementing systems are used (DCS – dual-cured bonding agents / dual-cured resin cements). However, few reports exist regarding the effectiveness of DCS when dual-cured bonding agents are left in the uncured state before the seating of the indirect restoration. Therefore, the aims of this study were: 1- to evaluate the microtensile bond strength (MTBS) and micromorphology of the adhesive interface of indirect restorations by confocal laser microscopy (CLSM) when the dual-cured bonding agents were left in the uncured state; 2- to analyze the degree of conversion (DC) by Fourier Transformed Infrared Spectroscopy and the bond strength of indirect restorations when DCSs were applied to the tooth and light activated or allowed to self-cure; 3- to evaluate the DC and ultimate tensile strength (UTS) of bonding agents light-activated with light curing units (LEDs and halogen light). The MTBS and UTS were analyzed using microtensile bond strength test. Different dyes were incorporated to the DCSs before they were applied to teeth for the CSLM analysis. For the DC analysis, the DSCs were applied to the diamond surface of attenuated total reflectance unit of the infrared device. The DC of the bonding agents related to the study evaluating the effectiveness of light-curing units was obtained from thin resin adhesive films. The results demonstrated that the MTBS was not affected, and the values were even higher for one 4th generation DCS, when the dual-bonding agents were left in the uncured state before the resin cement application. The CLSM analysis exhibited some variation in the micromorphological features, which depended on the DCSs and on the curing modes of bonding agents and resin cements. Some DCSs showed lower DC when pre-cured resin composite discs were used. The self-cured groups exhibited lower MTBS than the light-activated ones, except for one 4th generation DCS. The LED promoted lower DC in all bonding agents than did the halogen light. No difference in UTS was observed when LED was used. It was concluded that leaving the dual-cured bonding agent in the uncured state before seating the indirect restoration may be a reliable technique to ensure adequate MTBS, but most DCSs should be light-activated after seating the indirect restoration to provide optimal bond strength. Some LEDs can compromise the DC of adhesive systems.

Keywords: Dentin-bonding agents, Resin cements, Polymerization, Tensile strength, Dentin.

SUMÁRIO

PREFÁCIO

Esta tese está baseada nos seguintes artigos:

1. Effect of curing mode on microtensile bond strength to dentin of two dual-cured adhesive systems in combination with resin luting cements for indirect restorations. **Operative Dentistry, 2006, 32-1, 37-44**

2. Micromorphology of resin-dentin interface using 4th and 5th generation dual-cured adhesive / cement systems: a confocal laser scanning microscope analysis.

3. Effect of curing mode on the polymerization characteristics of dual-cured resin cement systems. **Submitted to Dental Materials**

4. *Microtensile bond strength of dual-polymerizing cementing systems to dentin using different polymerizing modes.* **Accepted for publication on the Journal of Prosthetic Dentistry**

5. *Degree of conversion of adhesive systems light-cured by led and halogen light.* **Brazilian Dental Journal (*in press*)**

1. INTRODUÇÃO GERAL

A indicação e utilização de restaurações indiretas em porcelana ou compósito têm crescido consideravelmente nos últimos anos. Além da melhora nas propriedades mecânicas desses materiais restauradores, como o aumento na resistência ao desgaste, na resistência à compressão e flexão (Leinfelder, 2005; Manhart *et al.*, 2004; Raigrodski, 2005; van Dijken, 1994), o desenvolvimento e aprimoramento dos sistemas de cimentação (agentes de união / cimentos resinosos) contribuiu para uma melhor união das restaurações indiretas à estrutura dental, promovendo maior segurança aos clínicos no momento da cimentação (Inokoshi *et al.*, 1993; Sjogren *et al.*, 1995).

Devido à presença da restauração indireta, a intensidade de luz que atravessa a restauração é reduzida consideravelmente (Rasetto *et al.*, 2004; Versluis *et al.*, 2004), o que pode resultar em baixo grau de conversão e conseqüentemente afetar as propriedades mecânicas da interface de união (Ruyter & Oysaed, 1982; Strang *et al.*, 1987). Por este motivo, foram desenvolvidos cimentos resinosos de dupla ativação. Além de apresentarem aminas aromáticas e fotoiniciadores como a canforoquinona para iniciarem a reação de polimerização através da ativação por luz, tais materiais apresentam também em sua composição peróxido de benzoíla e aminas terciárias, que geram radicais livres para que a reação de polimerização ocorra mesmo na ausência da fonte de luz (Milleding, 1992; Nathanson, 1987).

Preocupados em melhorar a qualidade dos equipamentos de fotoativação, alguns fabricantes têm se voltado para o desenvolvimento de fotoativadores equipados com diodos emissores de luz azul (LED). Por apresentarem comprimento de onda em torno de 470 nm, valor necessário para a ativação da canforoquinona, este tipo de equipamento dispensa o uso dos filtros utilizados nos fotoativadores com lâmpada halógena. Além disto, por possuírem semicondutores para a emissão de luz, as unidades de fotoativação de LED apresentam longa vida útil e as primeiras gerações de unidades de LED não geravam calor (Fujibayashi *et al.*, 1996).

Apesar dos constantes esforços na busca pelo desenvolvimento destes novos fotoativadores, os resultados da utilização das unidades de LED para fotoativação de compósitos têm se mostrado controversos. Nomura *et al.* (2002) observaram que os LEDs promoviam maior grau de conversão em compósitos, além da polimerização em camadas mais profundas. Knezevic *et al.* (2001), por sua vez, notaram que as unidades fotoativadoras contendo 18 LEDs promoviam valores de grau de conversão de compósitos inferiores aos obtidos utilizando fotoativadores contendo lâmpadas halógenas. Diante de tamanha controvérsia, nenhum autor tem questionado a eficiência de tais unidades de fotoativação na conversão em polímeros de monômeros resinosos de sistemas adesivos.

Alguns autores têm demonstrado que monômeros com baixo pH presentes em sistemas adesivos auto-condicionantes e até mesmo em sistemas de condicionamento total de frasco único apresentam incompatibilidade química com cimentos resinosos de dupla ativação, com compósitos autopolimerizáveis e até fotoativados (Giannini *et al.*, 2004; Sanares *et al.*, 2001; Tay *et al.*, 2003; Yamauchi, 1986). Essa reação adversa pode afetar a ação dos catalisadores redox binários peróxido-amina e conseqüentemente comprometer a resistência de união de restaurações indiretas quando a luz utilizada na fotoativação é atenuada ou ausente durante a polimerização desses sistemas de fixação, a qual passa a depender exclusivamente da reação química de ativação (Giannini *et al.*, 2004; Sanares *et al.*, 2001; Tay *et al.*, 2003; Yamauchi, 1986). Na tentativa de se eliminar tal incompatibilidade química, fabricantes tem adicionado co-iniciadores nos sistemas adesivos, como sulfinatos aromáticos de sódio, organoboro e ácido barbitúrico / cloreto cúprico (Ikemura & Endo, 1999). Tais componentes têm a função de reagir com monômeros resinosos de baixo pH para produzir radicais livres fenil e benzenosulfonil, os quais iniciam a reação de polimerização de materiais a base de resina de dupla ativação quando a luz proveniente do aparelho fotopolimerizador não é capaz de atingir o material restaurador (Ikemura & Endo, 1999; Wang *et al.*, 1999).

Mesmo com o desenvolvimento destes sistemas de união de dupla ativação, a maioria dos fabricantes recomenda a fotoativação do agente de união previamente à fixação da restauração indireta com o cimento resinoso. Considerando-se que nesta situação considerável intensidade de luz fotoativadora atinge a camada de adesivo, adequado grau de conversão dos monômeros na camada híbrida e da camada de adesivo pode ser obtido e como conseqüência maior resistência de união pode ser proporcionada (McCabe & Rusby, 1994). Entretanto, alguns estudos têm demonstrado que a espessura da camada de resina adesiva polimerizada pode interferir na adaptação marginal da restauração indireta (Frankenberger *et al.*, 1999; Hahn *et al.*, 2000; Pashley, 1991). Além disso, a camada adesiva criada por agentes de união de 5ª geração, também conhecidos como sistemas de frasco único com condicionamento ácido separado, os quais contêm água, solventes orgânicos e alto conteúdo de monômeros hidrófilos, pode apresentar-se mais susceptível á degradação hidrolítica do que as camadas contendo maior quantidade de monômeros hidrófobos, como aquelas criadas por sistemas de união de 4ª geração, conhecidos como adesivos com *primer* e a resina fluida hidrófoba colocados em frascos separados (De Munck *et al.*, 2003; Tanaka *et al.*, 1999).

No intuito de eliminar tais limitações, outra alternativa de cimentação de restaurações indiretas tem sido proposta: a aplicação do cimento resinoso e fixação da peça sobre o agente de união não polimerizado. Embora alguns estudos tenham demonstrado que a pressão da cimentação da peça protética possa colabar as fibrilas colágenas da dentina desmineralizada (Dietschi & Herzfeld, 1998; Magne & Douglas, 1999), esta técnica de fixação permite melhor adaptação da restauração indireta (Frankenberger *et al.*, 1999) e pode criar uma camada combinada composta pela mistura do agente de união e do cimento resinoso ao invés de uma camada composta apenas por resina adesiva. Esta nova camada combinada produz maior concentração de monômeros hidrófobos oriundos do cimento resinoso, fator este que poderia prolongar a durabilidade da interface de união adesiva (De Munck *et al.*, 2003; Tanaka *et al.*, 1999), principalmente se tais componentes do cimento resinoso forem capazes de penetrar no interior da camada híbrida e elevar a concentração de monômeros hidrófobos. Entretanto, pouco se sabe a respeito desta mistura entre cimento resinoso e agente de união.

A utilização da microscopia de varredura confocal laser pode ser utilizada para averiguar a interação entre resinas adesivas e cimentos resinosos na superfície dentinária e até mesmo no interior da camada híbrida. Este método permite a precisa localização de corantes de marcação ou fluorocromos adicionados em materiais resinosos (D'Alpino *et al.*, 2006a; D'Alpino *et al.*, 2006b). Deste modo, a microscopia confocal laser é capaz de excitar seqüencialmente diferentes fluorocromos com comprimentos de ondas seletos para cada corante. Como conseqüência, diferentes fluorocromos com espectros de emissão distintos misturados aos componentes resinosos aplicados na dentina permitem a localização precisa da resina adesiva e do cimento resinoso na interface de união.

Uma forma de se avaliar a efetividade dos co-iniciadores de agentes de união duais em conjunto com cimentos resinosos de dupla ativação consiste na análise do grau de conversão de tais componentes aplicados juntos ou separadamente, utilizando-se a Espectroscopia Infravermelha Transformada de Fourier. Através deste método, é possível averiguar a porcentagem de ligações duplas alifáticas de carbono previamente e após polimerização do material resinoso, proporcionando a porcentagem relativa da conversão dos monômeros em cadeias poliméricas (Rueggeberg *et al.*, 1990; Ruyter & Svendsen, 1978; Ruyter, 1981). Deste modo, a análise cinética e final do grau de conversão bem como a análise das propriedades mecânicas dos sistemas adesivos duais juntamente com cimentos resinosos após a fotoativação direta, após a exposição por intensidade reduzida de luz e após autopolimerização, pode estabelecer evidências a respeito da efetividade destes sistemas nas mais adversas situações clínicas.

2. PROPOSIÇÕES GERAIS

Os objetivos deste estudo foram:

1. Avaliar através do ensaio de microtração a resistência de união de sistemas de cimentação de dupla ativação quando os agentes de união de dupla ativação são fotoativados ou mantidos na forma não polimerizada previamente a aplicação dos cimentos resinosos, os quais foram fotoativados ou não após a cimentação da restauração indireta.

2. Analisar através da microscopia de varredura confocal laser e microscopia eletrônica de varredura a interface de união de sistemas de cimentação de dupla ativação quando os agentes de união são fotoativados ou mantidos na forma não polimerizada previamente à aplicação dos cimentos resinosos e a restauração indireta é submetida ou não a fotoativação.

3. Avaliar através da Espectroscopia Infravermelha Transformada de Fourier o grau de conversão de sistemas adesivos de dupla ativação aplicados juntamente com cimentos resinosos de dupla ativação na simulação de diferentes condições clínicas em que a luz fotoativadora é consideravelmente atenuada ou ausente.

4. Avaliar através do ensaio de microtração a resistência de união de sistemas de cimentação de dupla ativação de quarta e quinta gerações quando os agentes de união de dupla ativação não são polimerizados previamente a aplicação dos cimentos resinosos e a restauração indireta é submetida ou não a fotoativação.

5. Avaliar através da Espectroscopia Infravermelha Transformada de Fourier o grau de conversão de um sistema adesivo de frasco único e um auto-condicionante fotoativados com luz halógena ou LED.

3.CAPÍTULOS

Esta tese está baseada na Resolução CCPG/001/98/UNICAMP que regulamenta o formato alternativo para teses de Mestrado e Doutorado, e a declaração dos autores permitindo a inserção de artigos científicos publicados por outras editoras pode ser encontrada no Anexo 5. Deste modo, esta tese é composta por cinco capítulos contendo artigos submetidos e/ou aprovados para publicação, conforme descrito abaixo:

Capítulo 1:

Effect of curing mode on microtensile bond strength to dentin of two dual-cured adhesive systems in combination with resin luting cements for indirect restorations. ***Operative Dentistry, 2006, 32-1, 37-44***

Capítulo 2:

Micromorphology of resin-dentin interfaces using 4th and 5th generation dual-cured adhesive / cement systems: a confocal laser scanning microscope analysis

Capítulo 3:

Effect of curing mode on the polymerization characteristics of dual-cured resin cement systems. **Submitted to Dental Materials**

Capítulo 4:

Microtensile bond strength of dual-polymerizing cementing systems to dentin using different polymerizing modes. **Accepted for publication on the Journal of Prosthetic Dentistry**

Capítulo 5:

Degree of conversion of adhesive systems light-cured by led and halogen light. **Brazilian Dental Journal (*in press*)**

EFFECT OF CURING MODE ON MICROTENSILE BOND STRENGTH TO DENTIN OF TWO DUAL-CURED ADHESIVE SYSTEMS IN COMBINATION WITH RESIN LUTING CEMENTS FOR INDIRECT RESTORATIONS

CA ARRAIS • M GIANNINI • FA RUEGGEBERG • DH PASHLEY

*University of Campinas, Piracicaba School of Dentistry, Department of Restorative Dentistry, Av. Limeira, 901, Piracicaba, SP, 13414-018.

César Augusto Galvão Arrais, DDS, MS, Doctoral Student*
Marcelo Giannini, DDS, MS, PhD, Associate Professor*
Frederick A. Rueggeberg, DDS, MS, Professor and Section Director, Department of Oral Rehabilitation, School of Dentistry, Medical College of Georgia, Augusta, 1120, 15th Street, Room AD 3265, Georgia, USA.
David H. Pashley, DMD, PhD, Professor, Department of Oral Biology and Maxillofacial Pathology, Medical College of Georgia, 1459, Laney Walker Blvd, Room 2118, Augusta, Georgia, USA.

Corresponding author:
Corresponding author: Marcelo Giannini
Department of Restorative Dentistry/Operative Dentistry
Piracicaba School of Dentistry, UNICAMP
Av. Limeira, #901, Piracicaba, SP, 13414-900– Brazil
Telephone: 55 1934125338
Fax: 55 1934125218
E-mail: giannini@fop.unicamp.br

SHORT TITLE

Effect of curing mode on bond strength of dual-cured resin adhesive/cement systems

CLINICAL RELEVANCE

The separate step of light-curing of the adhesive resin component of some 4th and 5th generation dual-cured adhesive systems may be eliminated prior to cementation of an indirect resin composite restoration without deterioration in microtensile bond strength.

ABSTRACT

This study evaluated the microtensile bond strength (μTBS) of dual-cured adhesive systems when the different components were either light-activated or left in the uncured state prior to cementation of an indirect composite restoration. Occlusal dentin surfaces of forty human third molars were flattened. Teeth were randomly assigned into 8 groups (n=5) according to the dual-cured systems (bonding agents/resin cements) and curing modes: All Bond 2/Duolink (AB2-Bisco Inc.) and Optibond Solo Plus Dual Cure/Nexus 2 (SOLO-Kerr). Resin cements were applied to pre-cured resin composite discs (2 mm thick/Z-250/3M ESPE), which were fixed to dentin surfaces containing adhesive resin in either cured (LP) or uncured states (SP). The restored teeth were light-activated according to the manufacturers' instructions (LRC - XL3000/3M ESPE) or allowed to self-cure (SRC). Restored teeth were water-stored at 37° C for 24 h. Teeth were then both mesial-distally and buccal-lingually sectioned to obtain bonded specimens (1.2 mm^2). Each specimen was tested in tension at a crosshead speed of 0.6 mm/min until failure. Data (MPa (SD)) were analyzed by 2-way ANOVA and Tukey's post-hoc test ($P<.05$). AB2/SP exhibited higher μTBS than AB2/LP ($p=.00001$); however, no significant differences were noted between SOLO/LP and SOLO/SP. Results suggested that dual-cured adhesive systems were as strong or even stronger when they were left in the uncured state prior to indirect resin composite cementation.

INTRODUCTION

Composite resin and ceramic inlay/onlay restorations are advocated as alternative to metal restorations because of increasing esthetic demand and advancements in adhesive dentistry.[1,2] Clinical success of composite and ceramic indirect restorations is attributed to the reliable bond between adhesive cementing systems (resin cements / bonding agents) and mineralized dental tissues.[3,4] However, as light intensity reaching the resin cement is strongly attenuated by either the distance from the light source or from the absorbing characteristics through the indirect restorative material,[5] dual-cured resin materials have been developed.[6,7]

Dual-cured systems consist of a mixture between monomers and catalysts, and are formulated so as not to depend solely on light activation for proper cure. Therefore, light activation of such systems prior to delivering an indirect restoration might not be necessary. This method of indirect restoration placement on the uncured resin cement and adhesive resin layer is usually recommended in an attempt to ensure an adequate marginal adaptation and to avoid incomplete seating of the restoration, which are the primary concerns of clinicians.

The pressure from luting composite during seating of an inlay/onlay may cause a collapse of demineralized collagen fibers when the adhesive applied to dentin is not previously polymerized.[8] In addition, by evaluating *in vitro* occlusal wear, quantity of remaining double bonds and hardness, some authors indicated that the chemical curing mechanism alone is less effective than the light-activated one when dual-cured restorative materials are used.[9-11] Based on this evidence, some manufacturers recommend light activation of dual-cured adhesive systems prior to applying resin cement and seating the restoration on the prepared tooth. However, the difference in bond strength between these two clinical techniques for cementation of indirect restorations when dual-cured adhesive systems are used has yet to be evaluated.

The purpose of this study was to evaluate the microtensile bond strength (μTBS) of a 4th and a 5th generation dual-cured dentin bonding agents (adhesive resins) combined with their respective dual-cured resin cements when each is either allowed to self-cure or is exposed to light through a pre-cured disc of resin composite. In addition, the failure site morphology is classified and compared with respect to materials and curing mode type. The research hypothesis was that the independent light activation of both resin adhesive and resin cement would result in significantly higher bond strengths than when either is allowed to self-cure only. In addition, it was expected that bond strengths will be better when manufacturer instructions are followed.

MATERIAL AND METHODS

Indirect Restorative Bonding Procedures

Forty freshly extracted, erupted human third molars, which were stored in saturated thymol solution at 5°C for no more than three months**,** were used following a protocol approved by the Human Assurance Committee at The Medical College of Georgia (HAC #0403333). Teeth were transversally sectioned in the middle of the crown using a diamond blade (Series 15HC Diamond, number 11-4244; Buehler Ltd., Lake Bluff, IL, USA) on an automated sectioning device (Isomet 2000; Buehler Ltd.) under water irrigation, exposing areas of middle depth dentin. The exposed dentin surfaces were wet-polished by machine (Supermet Grinder, item #48-1581, Buehler Ltd.) with 600-grit SiC paper (pn 810-281-PRM, Silicon Carbide PSA Discs, Leco Corp., St. Joseph, MI, USA) to create a flat surface with standard smear layer formation before being bonded with the adhesive systems. Prepared teeth were randomly divided into eight groups (n = 5 specimens per group).

Commercial forth- and fifth-generation dual-cured dentin adhesive systems were used (Table 1). The corresponding dual-cured resin cements from each manufacturer were also applied (Table 1). Forty light-activated composite resin discs (2-mm thick and 10 mm in diameter – A2 shade – Z250, lot# 5LB; 3M/ESPE, St. Paul, MN, USA) were prepared to simulate overlying laboratory-processed composite resin restorations. The surface of each pre-cured resin disc that was to be bonded was sandblasted with 50 μm aluminum oxide particles (lot # 51116150, micron white, Danville Engineering Inc., San Ramon, CA, USA) for 10 s (air pressure: 80 psi; distance from the tip: 1.5 cm) (Comco MB 1002; COMCO Inc., Burbank, CA, USA). All adhesive systems and resin cements were manipulated and applied to the dentin surfaces according to manufacturers' instructions (control): light activation (20 s, light intensity: 550 – 630 mW/cm^2, XL3000, sn #202149; 3M/ESPE) of the Primer A and B mixture of All Bond 2 (Bisco Inc., Schaumburg, IL, USA), as well as the mixture of Optibond Solo (Kerr Corp., Orange, CA, USA) and the activator component prior to placement of the respective resin cements (Table1). For the experimental groups, all adhesive systems were applied and left in the uncured state, relying totally on any self-curing mechanism.

The mixed resin cement pastes were applied to the pre-cured composite disc following manufacturers' instructions and the disc was positioned and fixed to the adhesive-coated dentin surface under load of 500 g for 5 min, during which the resin cement was allowed to self-cure. When the cementing materials were light-activated through the pre-cured composite disc, the curing unit tip was positioned against the composite disc and each sample was exposed to 40 s (XL 3000, 3M/ESPE). A 2-mm thick block of self-curing resin composite (lot #0500006449, shade A3/A3.5, Bisfil 2B, Bisco Inc.) was then added to the untreated, cured composite surface to allow easier specimen manipulation while the mechanical test was performed. For groups where resin cements were self-cured, the block of self-curing resin composite was applied to the composite disc only after the time stipulated for the cement's self-cure reaction to complete.

Microtensile Bond Strength Test (µTBS)

Restored teeth were stored in distilled, deionized water at 37°C for 24 h and were vertically, serially sectioned into several 0.8-mm thick slabs using the same cutting instrument previously mentioned. Each slab was further sectioned to produce bonded sticks of approximately 1.2 mm^2. Each bonded stick was attached to the grips of a microtensile testing jig (Bisco Inc.) with cyanoacrylate cement (Zapit, Dental Ventures of America Inc., Corona, CA, USA) and tested in tension on a universal testing machine (Vitrodyne V1000 Universal Tester, Chatillon, Greensboro, NC, USA) at a cross head speed of 0.6 mm/min until failure. After testing, the specimens were carefully removed from the fixtures with a scalpel blade and the cross-sectional area at the site of fracture was measured to the nearest 0.01 mm with a digital micrometer (Series 406; Mitutoyo America Corp., Aurora, IL, USA). Specimen cross-sectional areas were calculated in order to present µTBS data in units of stress: MPa.

Statistical Analysis

A two-way analysis of variance (ANOVA) (effect of adhesive resin curing mode, effect of resin cement curing mode) was performed for each dual-cured adhesive system because the purpose of this study was not to compare product strengths, but to evaluate curing mode techniques. Tukey's post-hoc test was used to detect pair-wise differences within a bonding system. All statistical testing was performed at a pre-set alpha of 0.05.

Failure pattern analysis

Fractured surfaces of tested specimens were allowed to dry overnight at 37^{o} C. The surfaces were sputter-coated with gold (Model EMS-76M, Fullan Corp., NY, USA) and observed under a scanning electron microscope (XL-30, Philips. Hillsboro, OR, USA). Failure patterns were classified as follows: at the resin cement-adhesive layer interface, cohesive within the resin cement, adhesive along the pre-cured composite overlay-resin cement interface, adhesive either within or at the top of the hybrid layer and adhesive resin layers, and mixed when simultaneously exhibiting remnants of both hybrid layer and resin cement.[12]

RESULTS

Microtensile Bond Strength Test

The µTBS results are displayed in Table 2. When All Bond 2 was applied, light activation of the primer resulted in more than 50% lower µTBS values than when the primer was not light-activated before the resin cement was applied (p<.0001).

The mode of resin cement cure did not affect μTBS regardless of the mode of primer layer cure.

On the other hand, when Optibond Solo Plus Dual Cure was used, no significant difference in μTBS was observed when the adhesive resin layer was light-activated or left in the uncured state. However, the mode of resin cement cure affected the tensile bond strength regardless of the mode of cure of the adhesive resin ($p=0.0036$): 24.7% (for light-activated adhesive resin) and 46.4% (for self-cured resin) higher μTBS when the resin cement was light-activated than when it was allowed to self-cure.

Failure pattern analysis

Figure 1 shows the proportional prevalence (%) of the failure patterns in all experimental groups. For All Bond 2, the most predominant failure pattern was cohesive along the cement-adhesive interface when the primer was light-activated (Fig. 2). However, adhesive failure occurring either within or at the top of the hybrid layer and adhesive resin layers was the most predominant failure pattern when the primer was not light-activated separately (Fig. 3). Higher incidence of cohesive failure within the resin cement was observed when the resin cement was allowed to self-cure rather than when it was light-activated (Fig. 1).

An adhesive failure mode located either within or at the top of the hybrid layer and adhesive resin layers was also the most predominant failure pattern noted for Optibond Solo Plus Dual Cure when the adhesive layer was not independently light-activated and the resin cement was light-activated (Fig. 3). Failure at the cement-adhesive interface was predominantly observed when the adhesive layer was light-activated (Fig. 4). A mixed failure between resin cement and dentin surfaces was most commonly observed when both adhesive layer and resin cement were allowed to self-cure (Fig. 5).

DISCUSSION

The results of this study demonstrate that the method of curing mode used when cementing indirect composite restoration may affect tensile bond strength of indirect restorations depending on the cementing system used. Therefore, the research hypothesis that light activation of dual-cured adhesive systems would result in significantly higher bond strengths than when they are allowed to self-cure only was rejected. On the other hand, the research hypothesis that light activation of dual-cured resin cements would increase μTBS when compared to self-cured groups was accepted for Optibond Solo/Nexus2, but was rejected for All Bond 2/Duolink, regardless of the mode of cure established for the dual-cured adhesive systems.

Surprisingly, when used according to manufacturer' instructions (primer light-activated for 20 s), All Bond 2 exhibited lower μTBS than when the primer was left in the uncured state before seating the indirect restoration. This difference was unexpected since optimal primer polymerization (and thus physical properties) is expected when light exposing the resin adhesive directly. The failure pattern observed when the primer was light-activated and the resin cement was either light-activated or allowed to self-cure was predominantly located at the interface between the adhesive resin layer and the resin cement (Fig. 2). A similar failure pattern was observed by Mak et al.[12] when All Bond 2 was applied to dentin and an indirect composite onlay was cemented with resin cement. According to the authors, the failure pattern observed may be attributed to the inclusion of a high concentration of butylated hydroxytoluene (BHT), a polymerization inhibitor present in the adhesive resin (Pre-Bond) for the purpose of controlling the accelerated rate of cure of the resin cement caused by the presence of tertiary amine-based resin monomers in Primer A. The reduction in reaction speed by chemical inhibition occurs as free radicals are terminated by reacting with the phenolic hydrogen of the BHT molecule.[13] Therefore, it is possible that the decrease in available free radicals when Pre-Bond was combined with resin cement may have impaired the polymerization reaction of Duolink even when the resin cement was light-activated.

Although the manufacturer recommends that the primer must be light-activated for 20s, the µMTB of All Bond 2 without primer light activation was significantly higher than that obtained when the manufacturer's instructions were followed. The possible explanation for this finding may be related to the mixture among the primer and adhesive resin components within the hybrid layer when Pre-Bond is applied to the primed surface. Composed of a high concentration of hydrophobic monomers, such as Bis-GMA (Table 1), Pre-Bond adhesive resin may create a hybrid layer with high concentration of hydrophobic monomers and consequently lower hydrophilicity[14,15,16], improving its mechanical properties.[17,18] Moreover, dual-curing mechanisms within the hybrid layer may have contributed to the higher µTBS when Pre-Bond resin infiltrated the primed dentin surface. Considering that All Bond 2 Primer A contains a tertiary amine as a component for the self-curing reaction,[12] and Pre-Bond resin has benzoyl peroxide, it is possible that free-radicals within the hybrid layer might have been created not only from the light activation, but also from the self-curing redox reaction. As a consequence, a high content of free radicals may be available for the proper polymerization reaction to occur, even in the presence of high amount of BHT in Pre-Bond resin. Once the inhibitor is completely consumed, the polymerization reaction of the resin cement will proceed.

The research hypothesis for the effect of curing mode of dual-cured adhesive systems on µTBS proposed in this study was not accepted for Optibond Solo Plus Dual Cure. No differences in µTBS were observed when the adhesive system was either light-activated or allowed to self-cure before indirect resin composite cementation. The possible explanation for this finding may be related to the presence and effectiveness of a co-initiator component in the adhesive system. When the resin cement was applied to the uncured adhesive layer, the adhesive layer was replaced by a new combined layer, composed of a mixture of resin cement and adhesive resin. Without the presence of a co-initiator such as benzene sulfinic acid sodium salt, the tertiary amines from peroxide-amine component can react with acidic monomers to form a charge transfer complex (CT complex)[21] and loose their ability as reducing agents in redox reaction,[19,20,21,22] and a poor polymerization reaction would be expected from the combined adhesive/resin cement layer. However, when a separate co-initiator component is added to the adhesive resin, it reacts with the acidic monomers to form a phenyl free radical against the CT complex. For this reason, it is speculated that the combined adhesive/resin cement layer was allowed to self-cure properly when the co-initiator was included in the composition of Optibond Solo Dual Cure.

Other factors may have contributed to the high μTBS observed when Optibond Solo was not light-activated. When compared to the adhesive layer alone, the combined adhesive/cement layer would have higher filler content and more hydrophobic monomers, which would provide improved mechanical properties,[23] lower shrinkage,[24] and less susceptibility to hydrolytic degradation.[25] In addition, it is possible that the combined adhesive/cement layer is able to penetrate the entrance of dentinal tubules and increase the strength of the dentin bonding interface. Further studies are necessary to evaluate the micro-morphology of the dentin bonding interface created by indirect bonding procedures without light-activating the adhesive layer.

The effects of the resin cement curing modes on μTBS were also found to be material-dependent. For All Bond 2, the curing mode of Duolink did not affect the tensile bond strength, while lower μTBS was observed when Nexus 2 was allowed to self-cure after Optibond Solo was either light-activated or left in the uncured state. The evidence that the co-initiator of Optibond Solo was effective when Nexus 2 was applied to the light-activated adhesive layer may confirm that the self-curing mechanism by itself is ineffective to provide reliable mechanical properties to resin cements as previously reported.[9-11,26,27] This hypothesis was confirmed when fracture analysis of μTBS specimens revealed the failure pattern predominantly located at the bottom of the resin cement layer (Fig. 4).

Mixed failure exhibiting both the hybrid layer and regions with resin cement was the most predominant failure pattern observed when both adhesive resin and resin cement were allowed to self-cure (Fig. 5). This finding may indicate that the self-curing components were not able to provide high cohesive strength to the adhesive resin within the hybrid layer when the activating light is not available. This evidence is a matter of concern because weakly polymerized unfilled resins are more susceptible to an accelerated degradation process.[28,29] Further investigation is needed to evaluate the efficacy of the self-curing mechanism of dual-cured adhesive systems as well as the influence of the self-cure reaction of adhesive/cement layer on the polymerization of these adhesive resins.

The inclusion of an adhesive system without any self-curing or co-initiator components in this study could provide some indirect evidence regarding the effects of these self-curing components on the mechanical properties of the bonding interface. However, this study aimed only to evaluate how effective some specific dual-cured adhesive/resin cement systems are when indirect composite restorations are bonded to dentin. Thus, there is still a lack of information about the effectiveness and limitations of dual-cured bonding agents when they are used for indirect porcelain/composite restorations.

This study evaluated the effect of an alternative technique for indirect resin composite cementation when one 4th and one 5th generation dual-cured adhesive systems were used. As a comparison of products was deemed unimportant, only one 2-way ANOVA (mode of cure of resin cement factor; mode of cure of the adhesive systems factor) was performed for each product instead of a 3-way ANOVA including the products together. According to the study results, the alternative technique of allowing all components to self-cure provided μTBS equivalent to or significantly greater than that observed when the adhesive systems were light-activated. Therefore, this alternative technique for the 4th and 5th generation dual-cured adhesive systems may be a reliable option even in the worst clinical conditions where light exposure is totally compromised. However, further studies are necessary to confirm the effectiveness of other 4th and 5th generation dual-cured adhesive systems when no light exposure is available at all.

CONCLUSION

Within the limitations of this study, the following conclusions were observed:

1. The research hypothesis that the independent light activation of both adhesive resin and resin cement would result in significantly higher bond strengths than when either is allowed to self-cure only was rejected for the 4th generation dual-cured adhesive system evaluated. However, it was accepted for the 5th product only when the independent light-activation of both resin adhesive and resin cement values were compared to those obtained when the resin cement was allowed to self-cure, regardless of the curing mode of the adhesive resin.
2. When the manufacturers' instructions were followed, the bond strength values were either similar to or lower than those obtained when the alternative method of using self-curing for both adhesive and cement systems when delivering an indirect restoration.

Acknowledgments

The authors are indebted to Bisco Inc., Kerr Corp. and 3M ESPE Company for providing all restorative materials, to the Electron Microscopy Core Facility of the Medical College of Georgia for providing use of the microscopy facilities, and to the Medical College of Georgia School of Dentistry, USA. This study was supported by CAPES Brazil (BEX0184/05-5) and FAPESP (03/03645-0).

REFERENCES:

1. Dietschi D, Magne P & Holz J (1994) Recent trends in esthetic restorations for posterior teeth *Quintessence Int* 25(10) 659-677.

2. Martin JT (1994) Dental amalgam-what are the alternatives? *International Dental Journal* 44(303.

3. Inokoshi S, Willems G, Van Meerbeek B, Lambrechts P, Braem M & Vanherle G (1993) Dual-cure luting composites: Part I: Filler particle distribution *J Oral Rehabil* 20(2) 133-146.

4. Sjogren G, Molin M, van Dijken J & Bergman M (1995) Ceramic inlays (Cerec) cemented with either a dual-cured or a chemically cured composite resin luting agent. A 2-year clinical study *Acta Odontol Scand* 53(5) 325-330.

5. Strang R, McCrosson J, Muirhead GM & Richardson SA (1987) The setting of visible-light-cured resins beneath etched porcelain veneers *Br Dent J* 163(5) 149-151.

6. Milleding P, Ortengren U & Karlsson S (1995) Ceramic inlay systems: some clinical aspects *J Oral Rehabil* 22(8) 571-580.

7. Nathanson D (1987) Etched porcelain restorations for improved esthetics, part II: Onlays *Compendium* 8(2) 105-110.

8. Paul SJ & Scharer P (1997) The dual bonding technique: a modified method to improve adhesive luting procedures *Int J Periodontics Restorative Dent* 17(6) 536-545.

9. Blackman R, Barghi N & Duke E (1990) Influence of ceramic thickness on the polymerization of light-cured resin cement *J Prosthet Dent* 63(3) 295-300.

10. Hasegawa EA, Boyer DB & Chan DC (1991) Hardening of dual-cured cements under composite resin inlays *J Prosthet Dent* 66(2) 187-192.

11. Peutzfeldt A (1995) Dual-cure resin cements: in vitro wear and effect of quantity of remaining double bonds, filler volume, and light curing *Acta Odontol Scand* 53(1) 29-34.

12. Mak YF, Lai SC, Cheung GS, Chan AW, Tay FR & Pashley DH (2002) Micro-tensile bond testing of resin cements to dentin and an indirect resin composite *Dent Mater* 18(8) 609-621.

13. Braga RR & Ferracane JL (2002) Contraction stress related to degree of conversion and reaction kinetics *J Dent Res* 81(2) 114-118.

14. Van Meerbeek B, Conn LJ, Jr., Duke ES, Eick JD, Robinson SJ & Guerrero D (1996) Correlative transmission electron microscopy examination of nondemineralized and demineralized resin-dentin interfaces formed by two dentin adhesive systems *J Dent Res* 75(3) 879-888.

15. Van Meerbeek B, Yoshida Y, Snauwaert J, Hellemans L, Lambrechts P, Vanherle G, Wakasa K & Pashley DH (1999) Hybridization effectiveness of a two-step versus a three-step smear layer removing adhesive system examined correlatively by TEM and AFM *J Adhes Dent* 1(1) 7-23.

16. De Munck J, Van Meerbeek B, Yoshida Y, Inoue S, Vargas M, Suzuki K, Lambrechts P & Vanherle G (2003) Four-year water degradation of total-etch adhesives bonded to dentin *J Dent Res* 82(2) 136-140.

17. Dulik D, Bernier R & Brauer GM (1981) Effect of diluent monomer on the physical properties of bis-GMA-based composites *J Dent Res* 60(6) 983-989.

18. Asmussen E & Uno S (1993) Solubility parameters, fractional polarities, and bond strengths of some intermediary resins used in dentin bonding *J Dent Res* 72(3) 558-565.

19. Sanares AM, Itthagarun A, King NM, Tay FR & Pashley DH (2001) Adverse surface interactions between one-bottle light-cured adhesives and chemical-cured composites *Dent Mater* 17(6) 542-556.

20. Ruyter IE (1981) Unpolymerized surface layers on sealants *Acta Odontol Scand* 39(1) 27-32.

21. Bowen RL, Cobb EN & Rapson JE (1982) Adhesive bonding of various materials to hard tooth tissues: improvement in bond strength to dentin *J Dent Res* 61(9) 1070-1076.

22. Yamauchi J (1986) Study of dental adhesive containning phosphoric acid methacrylate monomer. *Japanese Journal of Dental Materials* 5(144-154.

23. Ferracane JL, Berge HX & Condon JR (1998) In vitro aging of dental composites in water--effect of degree of conversion, filler volume, and filler/matrix coupling *J Biomed Mater Res* 42(3) 465-472.

24. Labella R, Lambrechts P, Van Meerbeek B & Vanherle G (1999) Polymerization shrinkage and elasticity of flowable composites and filled adhesives *Dent Mater* 15(2) 128-137.

25. Calais JG & Soderholm KJ (1988) Influence of filler type and water exposure on flexural strength of experimental composite resins *J Dent Res* 67(5) 836-840.

26. Rueggeberg FA & Caughman WF (1993) The influence of light exposure on polymerization of dual-cure resin cements *Oper Dent* 18(2) 48-55.

27. Darr AH & Jacobsen PH (1995) Conversion of dual cure luting cements *J Oral Rehabil* 22(1) 43-47.

28. 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 *Dent Mater* 19(6) 458-465.

29. Schulein TM, Boyer DB & Chalkley Y (1984) Bond strength and hardness of light-activated composite resins *J Biomed Mater Res* 18(7) 789-796.

Table 1. Composition of the dual-cured adhesive systems used in this study

Product (Manufacturer)	Composition	Batch Number	Manufacturer's Instructions
All Bond 2 (Bisco Inc.)	*Primer A:* acetone; ethanol; Na-N-tolylglycine glycidylmethacrylate.	0500003574	Mix primers A and B. Apply 5 consecutive coats to dentin.
	Primer B: acetone; ethanol; biphenyl dimethacrylate.	0500003579	Dry all surfaces for 5-6 seconds with an air syringe.
	Pre-Bond Resin: Bis-GMA, TEGDMA; benzoyl peroxide; BHT	0500004345	Light-cure 20 seconds. Apply thin layer of Pre-Bond Resin immediately prior to cementation. Air thin. Do not light-cure!.
Duolink (Bisco Inc.)	*Base:* Bis-GMA; TEGDMA; glass filler; urethane dimethacrylate.	0500003751	
	Catalyst: Bis-GMA; TEGDMA; glass filler.		
Optibond Solo Plus Dual Cure (Kerr)	*Adhesive Resin:* ethyl alcohol; Bis-GMA; HEMA; GPDM; photoinitiators; barium aluminoborosilicate glass; fumed silica (silicon dioxide); sodium hexafluorosilicate.	428904	Dispense one drop of Optibond Solo Plus and Optibond Solo Activator into a disposable mixing well. Mix for 3s. Apply mixture to dentin with a light brushing for 15s to cover dentin surface.
	Activator: ethyl alcohol; alkyl dimethacrylate resins; benzene sulfinic acid sodium salt.	428260	Lightly air thin for 3s. Light-cure for 20s.
Nexus 2 (Kerr)	Monomers of methacrylic acid esters, Ba–Al –borosilicate glass, chemical and photoinitiators.	Base:423638 Catalyst:423975	

PENTA: dipentaerythritol penta acrylate monophosphate; HEMA: 2-hydroxyethyl methacrylate; BISGMA: bisphenol-A glycidyldimethacrylate TEGDMA: triethylene glycol dimethacrylate.

Table 2. μTBS of the 4th and 5th generation dual-cured adhesive systems:

Bonding System Generation (product)	Resin cement curing mode	Adhesive resin curing mode Light-activated	 Self-cured
4th Generation	Light (LRC)	14.6 (2.2)Aa	36.2 (5.6)Ab
(All Bond 2)	Self (SRC)	13.9 (1.8)Aa	37.8 (8.0)Ab
5th Generation	Light (LRC)	32.8 (4.9)Aa	34.1 (7.7)Aa
(Optibond Solo Dual Cure)	Self (SRC)	26.3 (6.9)Ba	23.7 (3.8)Ba

Groups having similar letters (upper case = column; lower case = row) are not significantly different. No cross comparisons between the two adhesives were made with regard to the 'column' statistical comparisons.

LEGENDS

Figure 1. Proportional prevalence (%) of failure patterns for all experimental groups.

Figure 2. Fractured specimen using All Bond 2, when primer was light-activated, exhibiting failure pattern classified as cohesive along the adhesive layer (AD) and resin cement (RC) interface (magnification 500X). This was the most predominant failure pattern observed when All Bond 2 was light-activated and the resin cement was either light- or self-cured and when Optibond Solo Plus Dual Cure was light-activated, but its resin cement was self-cured only.

Figure 3. Fracture located within the hybrid layer (HL) was the most predominant failure pattern for All Bond 2 when the primer was allowed to self-cure and for Optibond Solo Plus when the adhesive layer was left in the uncured state and the resin cement was light-activated (magnification 1500X).

Figure 4. Fractured specimen exhibiting cohesive failure pattern along the adhesive layer (AD) and resin cement (RC) interface (magnification 150X). This was the most predominant failure pattern observed when Optibond Solo Plus Dual-Cure was light-activated and its resin cement was self-cured.

Figure 5. Representative SEM photomicrograph of mixed failure pattern exhibiting resin cement (RC) and hybridized dentin surface (HL) (magnification 954X). This failure pattern was mostly observed when both adhesive resin and resin cement of Optibond Solo Plus/Nexus 2 were allowed to self-cure.

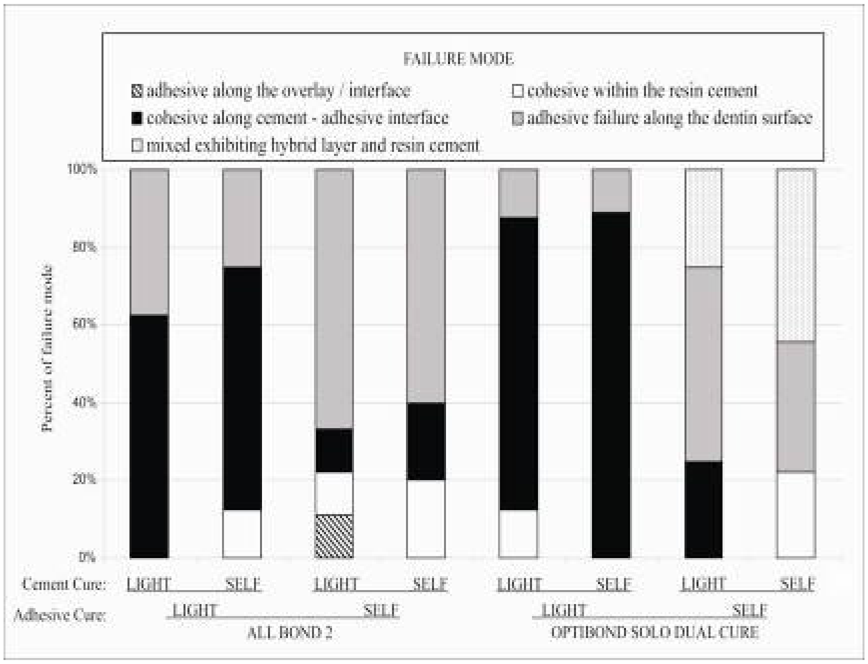


Figure 1

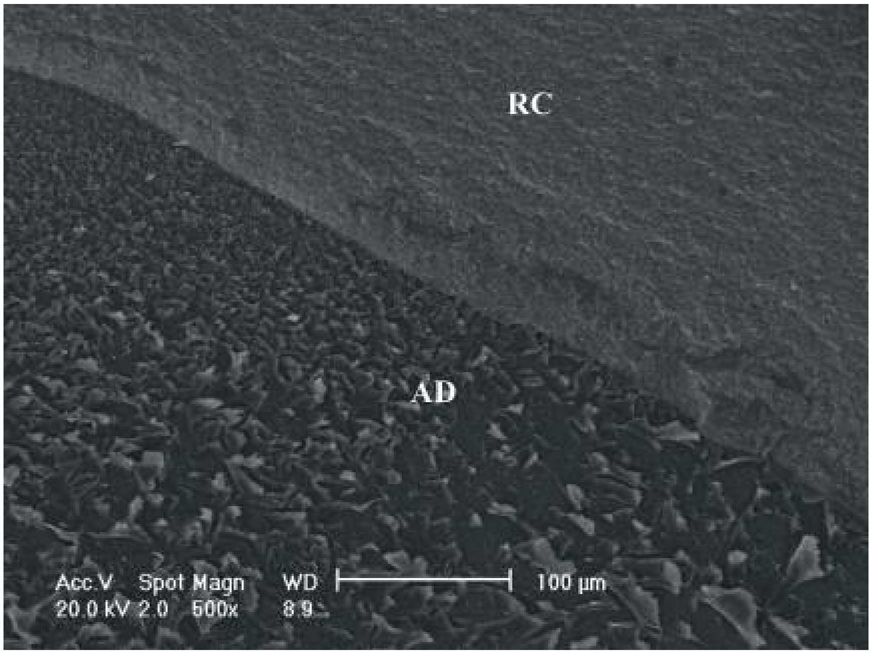


Figure 2

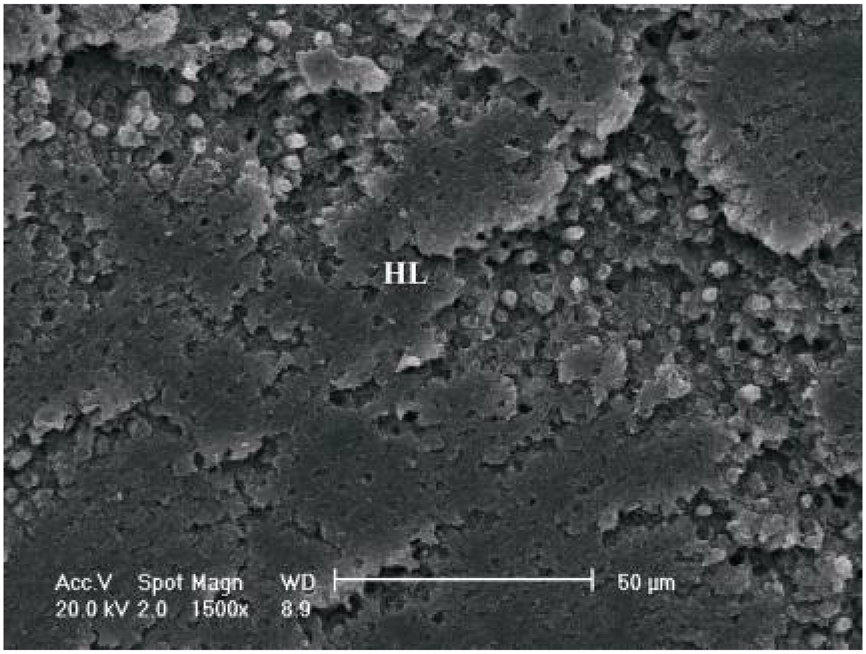


Figure 3

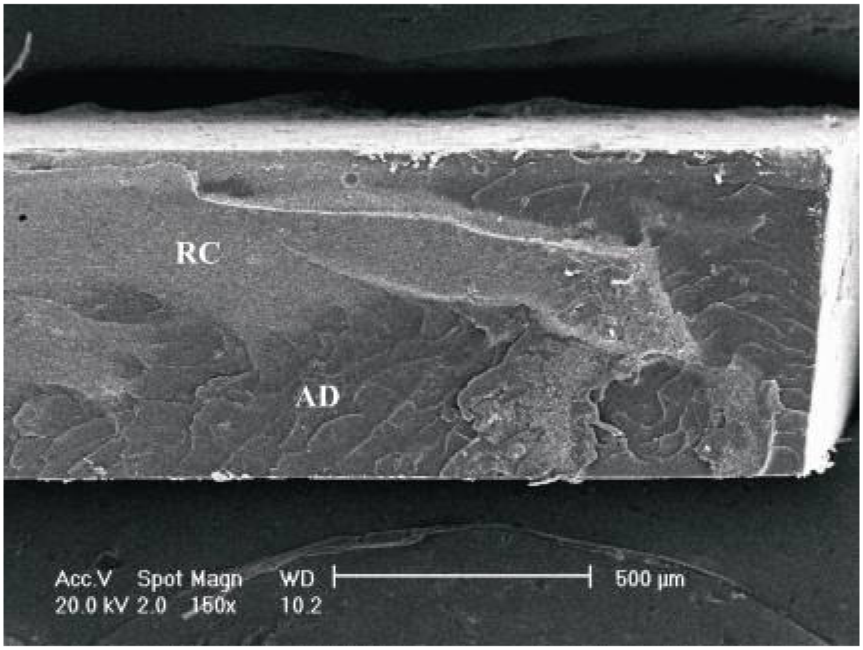


Figure 4

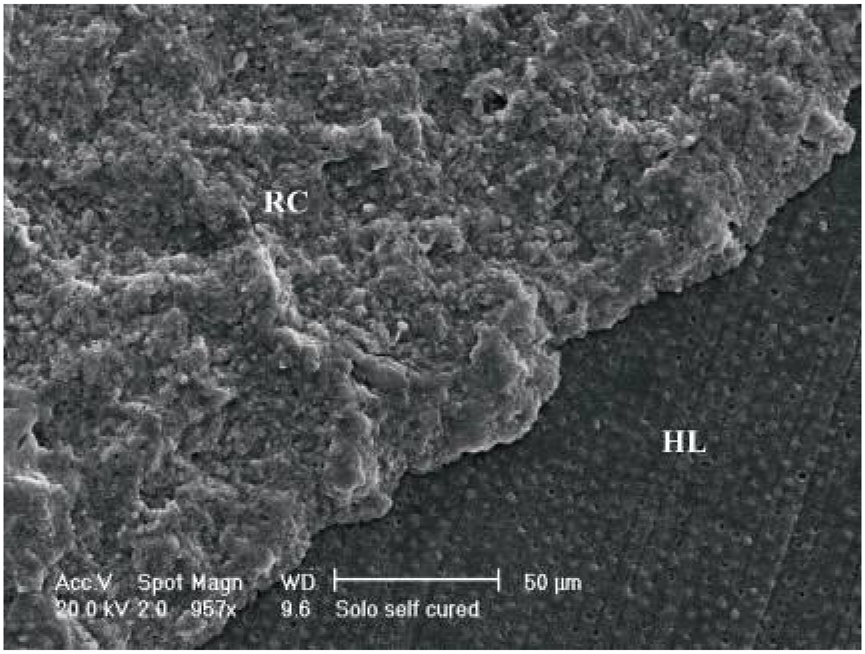


Figure 5

Micromorphology of resin-dentin interfaces using 4th and 5th generation dual-cured adhesive / cement systems: a confocal laser scanning microscope analysis

Cesar A.G. Arrais[a]/Katz Miyake[b]/Frederick A. Rueggeberg[c]/David H. Pashley[d]/Marcelo Giannini[e]

[a] DDS, MS, Doctoral Student, Department of Restorative Dentistry, Piracicaba School of Dentistry, State University of Campinas, Av. Limeira, 901, Piracicaba, SP, 13414-018, Brazil.

[b] PhD, Assistant Director Institute of Molecular Medicine and Genetics Medical College of Georgia, Augusta 1120 15th Street, Room CB 2815, Georgia, USA.

[c] DDS, MS, Professor and Section Director, Department of Dental Materials, School of Dentistry, Medical College of Georgia, Augusta, 1120, 15th Street, Room AD 3265, Georgia, USA.

[d] DMD, PhD, Professor, Department of Oral Biology and Maxillofacial Pathology, Medical College of Georgia, 1459, Laney Walker Blvd, Room 2118, Augusta, Georgia, USA.

[e] DDS, MS, PhD, Associate Professor, Department of Restorative Dentistry, Piracicaba School of Dentistry, State University of Campinas, Av. Limeira, 901, Piracicaba, SP, 13414-018, Brazil.

Corresponding author:

Corresponding author: Marcelo Giannini
Department of Restorative Dentistry/Operative Dentistry
Piracicaba School of Dentistry, UNICAMP
Av. Limeira, #901, Piracicaba, SP, 13414-900– Brazil
Telephone: 55 1934125338
Fax: 55 1934125218
E-mail: giannini@fop.unicamp.br

Keywords: Confocal Laser Scanning Mycroscopy; dual-cured adhesive systems; dual-cured resin cements; adhesive interfacial morphology; indirect restorations.

ABSTRACT

Purpose: This study evaluated the differential composition of resin-dentin interfaces of indirect restorations created by the application of 4th and 5th generation dual-cured cementing system (bonding agents/resin cements), when each material was either light-cured or allowed to self-cure.

Materials and Methods: Occlusal flat dentin surfaces of sixty human third molars were assigned into 12 groups (n=5) according to curing mode and dual-cured cementing system: 4th generation (AB2) All Bond2/Duolink (Bisco Inc.) and 5th generation (B1) Bond1/Lute-it (Pentron). Dextran Fluorescein (green) was mixed with the bonding agents, while Rhodamine (red) was incorporated into resin cements and Pre-Bond resin from AB2. Resin cements were applied to 2-mm thick pre-cured resin composite discs (Z250, 3M ESPE), which were fixed to dentin surfaces containing adhesive resin in either cured (light-cured; LC) or uncured (self-cured; SC) states. The restored teeth were light-activated (XL3000, 3M ESPE) according to the manufacturers' instructions (LRC) or allowed to self-cure (SRC), were stored for 24h and were vertically, serially sectioned into 1-mm thick slabs, which were analyzed using confocal laser scanning microscopy. Fluorescent additives provided indications of where individual components of the bonding/cement systems were located. Additional specimens were prepared and analyzed using scanning electron microscope.

Results: AB2/LC and B1/LC exhibited non-uniform primer/adhesive layer thickness. AB2/SC showed adhesive resin penetration within the primed dentin and resin cement penetration at the entrance of the dentin tubules. B1/SC/LRC exhibited resin cement penetration within the hybrid layer and into the dentin tubules. More intense resin cement penetration was observed in B1/SC/SRC groups.

Conclusion: The morphological features and component interactions among materials at resin-dentin interfaces are related to the activation modes of the primer/adhesive layer and of the resin cement.

INTRODUCTION

The demand for tooth-colored indirect restorations has grown considerably in the last years. The increase in this demand can be attributed to, among other factors, the reliable bond between adhesive cementing systems (resin cements / bonding agents) and mineralized dental tissues.[13,24] A stable and durable bond of indirect restorations to tooth is also related to a good marginal adaptation, which prevents microleakage, recurrent caries around restorations, and pulpal irritation.[26] In an attempt to improve marginal adaptation and bond strength of indirect restorations using 4th or 5th generation adhesive systems,[8,27] different luting procedures have been proposed.

The luting procedure for indirect restorations most recommended by manufacturers is based on light-activation of the adhesive resin before indirect restoration cementation. Because the bonding agent is accessible to direct light exposure, maximal polymer conversion and bond strength can be achieved.[16] However, some studies have demonstrated that a thick, cured adhesive layer can affect full seating, and thus marginal adaptation of indirect restorations.[9,11,17] Furthermore, cured adhesive layers created by 5th generation bonding agents usually contain residual water and high content of hydrophilic monomers, which make them more susceptible to hydrolytic degradation than layers containing more hydrophobic monomers and less residual water, such as those created by 4th generation adhesive systems.[6,28]

To overcome these limitations, another clinical approach was developed, in which the dentin bonding agent is left in the uncured state before application of the resin cement. Some studies demonstrate that the pressure of resin cement during cementation of a restoration may cause collapse of demineralized dentin.[7,15] However, this technique allows maximum restoration seating[9] and might create a combined adhesive layer composed of the mixture of bonding agent and resin cement. This new, combined layer would contain fewer hydrophilic monomers and more hydrophobic monomers from the resin cement components, improving the long-term durability of the bonded interface as a consequence.[6,28] However, no information exists regarding the creation of such a layer when dentin bonding agents are left in the uncured state before the resin cement application.

Confocal Laser Scanning Microscopy (CLSM) is well suited to study the presence of components from the bonding agent and resin cement on the dentin surface or even within the hybrid layer. This technique permits accurate co-localization of fluorescent markers that are incorporated to resinous materials. CLSM is capable of individually exciting different fluorochromes by applying selective wavelengths.[4,5] Fluorochromes with well-separated emission spectra mixed to the components allow analysis of the mixture and interaction between adhesive resin and resin cement components.

The purpose of this study was to evaluate the features of bonded interfaces of indirect resin composite restorations created by 4th and a 5th generation dual-cured dentin bonding agents combined with their respective dual-cured resin cements when each was either allowed to self-cure or was exposed to light through a pre-cured disc of resin composite. Visualization of specimen cross sections were made using both CLSM and scanning electron microscopy (SEM). The research hypotheses were that [1] when not light activated prior to resin cement application, the dentin bonding agent and resin cement components will be observed on the dentin surface and/or within the hybrid layer created by these materials used in their dual-cured form; and [2] light-activation of the bonding agent prior to cementation will produce a uniform adhesive layer and only a superficial mixture between adhesive and resin cement with no presence of resin cement at or within the hybrid layer.

MATERIAL AND METHODS

Adhesive resin preparation for Confocal Laser Scanning Microscopy

Commercial forth- and fifth-generation, dual-cured dentin adhesive systems and their corresponding dual-cured resin cements were used (Table 1). Dextran Fluorescein (batch No. 123K0723, Fluorescein–Isothiocyanate–Dextran, FD4, Sigma, St Louis, MO, USA) was incorporated into Primers A and B of All Bond 2

(40 µg/ml in each bottle) and into Bond 1 primer/adhesive resin (Pentron Corp., Wallingford, CT USA) (160 µg/ml in each bottle). Rhodamine B (Batch. 121K3688, RITC/Rhodamine B, R6626, Sigma, St Louis, MO, USA) was mixed with Pre-Bond resin of All Bond 2 (6.4 µg/ml) (Bisco Inc., Schaumburg, IL, USA), as well as with the dual-cured resin cements Duolink (0.32 µg/mg) (Bisco Inc.) and Lute-it (0.32 µg/mg) (Pentron Corp.). When added to the resin cements, the dye was incorporated to the base paste and was mixed with spatula until the base paste changed its shade uniformly. The dye-laden cement component was returned to the original syringe from which it was extruded. The dyes were added directly to the packages of the adhesive resins provided by the manufacturers and the solution containing dyes and adhesive resins was maintained in a stirring device (Vortex Machine, Scientific Industries, Inc., New York, NY, USA) for at least 2 h to provide complete dye dissolution

Indirect Restorative Bonding Procedures

Sixty freshly extracted, erupted human third molars, which were stored in saturated thymol solution at 5^{o} C for no longer than three months**,** were used following a protocol approved by the Human Assurance Committee at The Medical College of Georgia (HAC #0403333). Teeth were transversally sectioned in the middle of the crown using a diamond blade (number 11-4244, Series 15HC Diamond, Buehler Ltd., Lake Bluff, IL, USA) on an automated sectioning device (Isomet 2000, Buehler Ltd.) under water irrigation, exposing areas of middle depth dentin. The exposed dentin surfaces were wet-polished by machine (Supermet Grinder, item #48-1581, Buehler Ltd.) with 600-grit SiC paper (pn 810-281-PRM, Silicon Carbide PSA Discs, Leco Corp., St. Joseph, MI, USA) to create a flat surface with standard smear layer formation before being bonded with the adhesive systems.[29]

Sixty light-activated composite resin discs (2-mm thick and 10 mm in diameter, A2 shade, Z250, lot# 5LB, 3M ESPE, St. Paul, MN, USA) were prepared to simulate overlying laboratory-processed indirect composite resin restorations. The surface of each pre-cured resin disc that was to be bonded was sandblasted (air pressure: 80 psi; distance from the tip: 1.5 cm; Comco MB 1002, COMCO Inc., Burbank, CA, USA) with 50 µm aluminum oxide particles (lot # 51116150, micron white, Danville Engineering Inc., San Ramon, CA, USA) for 10 s.

Prepared teeth were randomly divided into twelve groups (n = 5). Flow charts of the fabrication of each specimen type are presented in Fig 1 and 2. All adhesive systems and resin cements were manipulated and applied to the dentin surfaces according to manufacturers' instructions (control): light activation (20 s, sn #202149, XL 3000, 3M ESPE), power density of 600 mW/cm^2 (as measured using a laboratory grade spectral radiometer (DAS 2100, Labsphere, Sutton, NH, USA) of the Primer A and B mixture of All Bond 2. The mixture of Bond 1 and the activator component was left in the uncured state prior to placement of the respective resin cements (Table 1). For the experimental groups of the 4th generation product, the mixture of primers A and B were applied and left in the uncured state, relying totally on any self-curing mechanism, and Bond 1 was light-activated for 20 s prior the resin cement application. The penetration pattern of Pre-Bond resin into the primed dentin when All Bond 2 was used was evaluated using four additional experimental groups, in which Rhodamine B was incorporated into the Pre-Bond resin instead of into the resin cement. (Fig 1)

The mixed resin cement pastes were applied to the pre-cured composite disc following manufacturers' instructions and the disc was positioned and fixed to the adhesive-coated dentin surface under load of 500 g for 5 min, during which the resin cement was allowed to self-cure. When the cementing materials were light-activated through the pre-cured composite disc, the curing unit tip was positioned against the composite disc surface and each sample was exposed to 40 s (XL 3000, 3M ESPE).

Confocal Laser Scanning Microscopy Analysis

The restored teeth were stored in vegetable oil for 24 h to prevent loss of water and dye and were vertically, serially sectioned into several 1-mm thick slabs using a diamond blade (Buehler Ltd., Lake Bluff, IL, USA) on a sectioning device (Isomet Low Speed Saw, Buehler Ltd, Evanston, IL, USA) under oil lubrication. The slabs were stored in vegetable oil for 24 h and were analyzed under CLSM (LSM 510 Meta Confocal Microscope, Zeiss, Göttingen, Germany). An argon laser at 488 nm and He–Ne laser at 543 nm provided the excitation energy. The intensity of the excitation light and the amplification of the photomultiplier were kept constant during the investigation period. CLSM images were recorded in fluorescent mode. The visualized layer was selected approximately 10 μm below the sample surface and images were recorded with an oil immersion objective (40X·, numerical aperture 1.3). The sizes of the recorded images were 230.3 X 230.3 μm^2 and 76.8 X 76.8 μm^2, and the resolution was 1024 X 1024 pixels. Images were recorded at magnifications of 770X and 3,000X from three different regions, on the bonded interface of each specimen. The different dyes provided specific emission wavelengths for each resinous component at the resin-dentin interface. Therefore, the mixture of primers A and B from All Bond 2 and Bond 1 emitted a green shade and Pre-Bond resin and the resin cements emitted red shade when they were excited by the lasers from the CLSM. Based on the fact that this was an observational evaluation, no statistical analysis was performed and only visual differences among experimental groups were considered as findings. The overall general appearance of the five replications from each experimental group were used to characterize trends seemed for that test condition.

Scanning Electron Microscopy Analysis

An additional 24 extracted, erupted human third molars were prepared, restored with the same dual-cured cementing systems and cured composite discs as described before, and were stored in water at 37^o C for 24 hours. The restored teeth were vertically sectioned in the middle using a diamond blade (Buehler Ltd., Lake Bluff, IL, USA) on a sectioning device (Isomet Low Speed Saw, Buehler Ltd, Evanston, IL, USA) to expose the resin dentin interface. The bonded interfaces were wet polished with 1200 and 2000 grit SiC paper and with 6 and 3 μm diamond pastes. A 5N HCl solution was applied to the specimen interfaces for 10 s to remove the inorganic components from the dentin surface. The specimens were washed with water, were immersed in 2.5% NaOCl for 10 min and were ultrasonicated for 1 min to remove all exposed collagen after treatment with acid, so only the hybrid layer and resin tags remained at the adhesive interface. Afterwards, the specimens were allowed to dry overnight at 37^o C, were sputter-coated with gold (MED 010, Balzer, Leichtenstein) and observed using a scanning electron microscope (VP 435, Leo, Cambridge, England) at the magnifications of 770 X and 3,000 X.

Results

Fig 3A, 3B, and 3C show CLSM images and 3D presents the SEM image of bonded interfaces created when All Bond 2 / Duolink was applied according to manufacturer's instructions, i.e., the mixture of primers A and B and the resin cement were each light-activated separately. The primer light-activation formed two different interfacial morphologies, one exhibiting a non-uniform primer layer (arrows - green shade, Fig 3A) and the other one showing the bonded interface without primer layer (Fig 3C). A yellow line was observed between the adhesive and resin cement layers (Fig 3B). When the primer layer was not evident on the SEM image (Fig 3D), it was noticed that the resin cement penetrated into the entrance of the dentinal tubules (asterisks - red shade – Fig 3C) and a red line was noted between the dentin surface and the resin cement layer (arrows). Similar morphological features were observed when All Bond 2 was applied according to the manufacturer's instructions and the resin cement was allowed to self-cure.

Fig 4A and 4B present the bonded interface created when All Bond 2 was applied to dentin, the mixture of primers A and B was left in the uncured state, and the resin cement was light-activated through the cures composite disc. Fig 4C shows SEM image from specimens restored following the same experimental protocol. In experimental group, fluorescein (green) was added to the primer and Rhodamine (red) was added to the resin cement. A superficial penetration of the resin cement was observed at the top of the hybrid layer (arrows - Fig 4B), and dark spots related to the presence of Pre-Bond resin were noted within the resin cement layer at the top of the dentin surface (asterisks - Fig 4A and 4B). SEM images demonstrated a thinner hybrid layer than that observed in CLSM images.

Fig 5A and 5B show the bonded interface using CLSM , Fig 5C presents the SEM image created when All Bond 2 was applied to the dentin surface and the primer was left in the uncured state and the resin cement was light-activated, but Rhodamine was added to the adhesive resin (Pre-Bond) instead of to the resin cement. Pre-Bond resin (red) penetrated into all dentin tubules at apparently the same depth, approximately 12 μm (Fig 5A), and changes in the red-shade from light to dark red were also observed at the adhesive/resin cement layer (asterisks, Fig 5B). A light orange shade area was noted at the top of the hybrid layer (arrows, Fig 5B), indicating the mixture between primer and Pre-Bond resin at the top of the hybrid layer. When compared to the hybrid layer in the CLSM image, the thinner hybrid layer present in the SEM image (Fig 5C) after acid-base challenge seemed to correspond to the hybrid layer region containing both primer and Pre-Bond resin.

Fig 6A and 6B show the bonded interfaces created by All Bond 2 / Duolink on the dentin surface when the mixture of primers A and B was left in the uncured state and the resin cement was allowed to self-cure. Fig 6C corresponds to the SEM images obtained from dentin restored following a similar experimental protocol. The penetration of resin cement was observed at the entrance of most dentin tubules (Fig 6A and 6B - arrows). However, no morphological evidences of the presence of the resin cement into the dentin tubules, such as the presence of filler particles at the entrance of the dentin tubules, were noted in SEM images (Fig 6C).

Fig 7A and 7B present CLSM images of the bonded interfaces, and 7C shows the SEM interface created when Bond 1 was left in the uncured state and the resin cement was light-activated through cured composite resin. The change in shade from green to light yellow, orange or even red represents the mixture between the bonding agent and the resin cement within the hybrid layer (Fig 7A and 7B). The SEM image indicates a hybrid layer thickness similar to that observed in the CLSM images; however, no evidences of mixed components were seen.

When Bond 1 was not light-activated and the resin cement was allowed to self-cure (Fig 8A and 8B), a darker red shade was observed at the bottom of the hybrid layer in comparison to the shade observed within the hybrid layer when the resin cement was light-activated (Fig 7A and 7B). Deeper penetration of resin cement components (red) were also observed into dentin tubules along the entire bonded interface (Fig 8A and 8B). It was possible to observe the filler particles within the resin cement layer (arrows), but no filler particles were noted the dentin tubules.

Fig 9A and 9B show the bonded interfaces using CLSM ,and 9C presents the SEM images created by Bond 1 / Lute-it when the adhesive and resin cement layers were each light-activated separately. A non-uniform adhesive layer was observed, which was thicker in some regions than in others (Fig 9A). Some regions exhibited thick adhesive layers (Fig 9B, approximately 22 μm) and the mixture between resin monomers from the oxygen-inhibited uncured adhesive and resin cement layers was noted along the whole interface (Fig 9B - orange line – arrows). Separate adhesive and hybrid layers were also evident in the SEM images. The same application technique of Bond 1 / Lute-it also created bonded interfaces without a separate adhesive layer above the hybrid layer (Fig 10A, 10B, and 10C). Those interfaces were characterized by resin cement infiltration at the top of the hybrid layer (Fig 10B – arrows) and at the entrance of the dentinal tubules (Fig 10C - asterisks).

DISCUSSION

The results of this study demonstrated that resin cement and bonding agent components created a combined, mixed layer on the dentin surface when both the 4th and 5th generation adhesive systems were applied to dentin and left in the uncured state. Therefore, the first research hypothesis was validated for the cementing systems. However, only the bonded interfaces created by the 5th generation bonding agent and its respective resin cement exhibited the new combined layer within the hybrid layer.

The bonded interfaces created by the 5th generation bonding agent differed from those created by the 4th generation cementing system All Bond 2 / Duolink, which exhibited penetration of resin cement components only at the entrance of the dentin tubules (Fig 4 and 6). The main feature of 4th generation bonding agents is the separate bottles containing primer and bonding resin, respectively. According to the manufacturer's instructions, Pre-Bond bonding resin must be applied to dentin after application and light-activation of the mixture of primers A and B. The adhesive resin is developed to link resin composite to primed dentin, and is composed of a high concentration of hydrophobic monomers, such as Bis-GMA (Table 1). This monomer may be responsible for the high viscosity observed in Pre-Bond resin. As can be observed in Fig 3, Pre-Bond resin combines with the resin cement during the seating of the indirect restoration. Therefore, it is possible to speculate that the presence of the viscous Pre-Bond resin impairs and slows resin cement diffusion through it and within the hybrid layer when the primer was left in the uncured state. This speculation may be confirmed by the evidence that an apparently deeper penetration of the resin cement at the entrance of the dentin tubules was observed when the resin cement was allowed to self-cure (Fig 6).

Surprisingly, the 5th generation dual-cured cementing system Bond 1 / Lute-it exhibited resin cement components not only into the dentin tubules, but also within the hybrid layer (Fig 7 and 8). The darker orange and red shades correspond to higher concentration and yellow represents lower concentration of resin cement components within the hybrid layer. Therefore, higher concentration of resin cement components were observed at the top of the hybrid layer and into the dentin tubules as well, and lower concentration of those components was observed at the bottom of the hybrid layer. The infiltration of such resin cement components within the hybrid layer can be attributed not only to the low viscosity of the 5th generation bonding agent Bond 1 (Pentron), but also to the low viscosity of Lute-it (Pentron) when compared to that of Duolink (Bisco). The resultant effects of this mixture between dentin bonding agent and resin cement components on the mechanical properties at the hybrid layer will depend on the chemical compatibility among components, monomer conversion, and curing mode as well.[22] However, assuming confluence, it would be reasonable to assume that presence of the more hydrophobic resins from the cement at and into the hybrid layer would substantially improve the physical properties of the polymer formed in those areas.

Self-curing components, or co-initiators, were added to these bonding systems to overcome the chemical incompatibility between dual-cured resin cements and acidic monomer from the bonding agents to occur.[12] Otherwise, the tertiary amines from peroxide-amine component can react with acidic monomers to form a charge transfer complex (CT complex)[2] and loose their ability as reducing agents in redox reaction.[21,22,32] As a consequence, a poor polymerization reaction would be expected from the combined adhesive/resin cement layer or from the mixture between the primer / adhesive oxygen-inhibited layer [19,21] and resin cement components at the top of the light-activated bonding agent layer. This mixture between the primer / adhesive oxygen-inhibited layer was represented by the light orange line between the primer / adhesive and resin cement layers (arrows) (Fig 3B and 9B). Therefore, this interaction between resin cement and bonding agent components is only acceptable when dual-cured adhesive systems are used, even when the primer / adhesive layer are light-activated prior to resin cement application.

When Bond 1 was applied to dentin and left in the uncured state (the manufacturer recommended condition), a significant change in shade within the hybrid layer was observed when self-cured resin cement groups were compared with the light-activated ones. A light yellow hybrid layer was observed when the resin cement was light-activated, while dark red hybrid layer was noted when Lute-it was allowed to self-cure. Such differences in shade are probably related to the longer resin cement setting time promoted by its self-polymerization, which can take several minutes.[18,20] Therefore, the longer setting time allowed deeper resin cement penetration within the hybrid layer and co-mixture of these compounds with those of the primer/adhesive material. This change in monomer composition within the hybrid layer may result in higher content of hydrophobic monomers, which can contribute to longer durability at not only the adhesive layer but also within the hybrid layer.[6,28]

A non-uniform adhesive layer, which was totally absent at some bonded interfaces, was observed when the primer / adhesive layers of both 4th and 5th generation bonding agents were light-activated before the indirect restoration was seated (Fig 3A, 3C, 9A and 9B). Therefore, the second hypothesis of the current study was invalidated. Although the 3-D features of the CLSM images do not provide a clear indication about differences in dentin tubuli density, it is possible that a thinner or absent primer /adhesive layer is related to the higher density of dentin tubules when the bonding agents were applied to deep dentin surfaces.[10] More primer / adhesive resin would be necessary at deep dentin to compensate its higher permeability due the higher dentin tubuli density, and consequently create a uniform layer on the dentin. On the other hand, the same amount of primer / adhesive resin may create a thick layer when applied to other dentin surfaces where tubuli size and density may be less (Fig 3B and 9B). The layer thickness observed in some regions (approximately 23 μm – Fig 9B) can compromise the internal adaptation of indirect restorations and, as a consequence, may promote a thicker luting space at some internal and marginal areas of the restoration.[9,11,17] Several clinical and *in vitro* investigations revealed the luting space as being the weakest part of a ceramic inlay restoration.[14,23,25] For these reasons, in order to avoid a non-uniform or thick polymerized adhesive layer (Fig 3B, 9B, and 9C), care must be taken when a gentle air stream is applied before light-activation, in order to create a uniform layer not only at the cavity surfaces, but also at the cavity angles. Moreover, careful visual analysis of the bonded cavity may allow the clinician to distinguish regions with thick adhesive layer before the light-activation.

The SEM analysis (Fig 3D, 4C, 5C, 6C, 7C, 9C and 10A) was a useful tool to distinguish and confirm the micromorphological structures observed at the adhesive interface of the CLSM images. The acid treatment (5 N HCl) combined with 2.5% NaOCl was used to provide clear observation of the hybrid layer morphology and resin tags: demineralization of dentin and removal of unprotected collagen fibril. However, other studies have demonstrated that specimen polishing and acid treatment can damage the micromorphology and change the composition of the hybrid layer.[3,30,31] On the other hand, as specimen preparation for CLSM analysis does not involve chemical superficial treatments, and imaging is obtained below the surface, the micromorphology of the adhesive interface is preserved.[1] Furthermore, the CLSM images provided detailed information about component distribution from the adhesive resin and resin cements at the resin cement layer and within the hybrid layer as well, while such distinctions were not possible using SEM analysis.

Based on the findings of this study, it is recommended that care must be taken when dual-cured 4th or 5th generation adhesive systems are applied and indirect restorations are cemented on bonded dentin. Much more knowledge is needed to reliably provide an adequate marginal adaptation and proper formation of a combined layer at the bonded interface. Further *in vivo* studies are needed to evaluate the effects of dentinal fluids under pulpal pressure on the penetration of dual-cured resin cements into dentin tubules and within the hybrid layer, as well as the clinical performance of the mixture created by dual-cured bonding agents and resin cements such as that observed in this study.

CONCLUSION

Within the limitations imposed in this study, the following conclusions may be made:

[1] A combined layer composed of primer / bonding agent and resin cement was observed on the dentin surface and at the entrance of the dentinal tubules when 4th generation dual-cured adhesive system was used; the 5th generation dual-cured bonding agent used created the combined layer not only on the dentin surface, but also within the hybrid layer and in the dentin tubules.

[2] Light-activation of the primer for All Bond 2 and bonding agent for Bond 1 before the cementation of indirect restoration provided a non-uniform adhesive

layer, which was also totally absent in some regions, and did not allow monomer infiltration from the resin cement or Pre-Bond resin into the hydrophilic bonding agent and dentin.

[3] The option of not light curing the bonding agent prior to the application of resin cement can be a reliable technique considering the changes in composition and morphology of the adhesive interface; however, only the evaluation of the mechanical properties of the adhesive interfaces created when this technique is used will confirm its effectiveness.

Acknowledgments

The authors are indebted to Bisco Inc. and the Pentron Corporation for providing all restorative materials, and to Dr. E. W. Kitajima (NAP-MEPA/ESALQ-USP) for support of microscopy procedures used. This study was supported by grants from FAPESP (#03/03645-0) and CAPES (#BEX 0184/05-5) and the Medical College of Georgia School of Dentistry, Augusta, GA, USA.

REFERENCES:

1.Bitter K, Paris S, Martus P, Schartner R, Kielbassa AM. A Confocal Laser Scanning Microscope investigation of different dental adhesives bonded to root canal dentine. Int Endod J 2004;37:840-848.

2.Bowen RL, Cobb EN, Rapson JE. Adhesive bonding of various materials to hard tooth tissues: improvement in bond strength to dentin. J Dent Res 1982;61:1070-1076.

3.Carvalho RM, Yoshiyama M, Horner JA, Pashley DH. Bonding mechanism of VariGlass to dentin. Am J Dent 1995;8:253-258.

4.D'Alpino PH, Pereira JC, Svizero NR, Rueggeberg FA, Pashley DH. Use of fluorescent compounds in assessing bonded resin-based restorations: A literature review. J Dent 2006.

5.D'Alpino PH, Pereira JC, Rueggeberg FA, Svizero NR, Miyake K, Pashley DH. Efficacy of composite surface sealers in sealing cavosurface marginal gaps. J Dent 2006;34:252-259.

6.De Munck J, Van Meerbeek B, Yoshida Y, Inoue S, Vargas M, Suzuki K, et al. Four-year water degradation of total-etch adhesives bonded to dentin. J Dent Res 2003;82:136-140.

7.Dietschi D, Herzfeld D. In vitro evaluation of marginal and internal adaptation of class II resin composite restorations after thermal and occlusal stressing. Eur J Oral Sci 1998;106:1033-1042.

8.Dong CC, McComb D, Anderson JD, Tam LE. Effect of mode of polymerization of bonding agent on shear bond strength of autocured resin composite luting cements. J Can Dent Assoc 2003;69:229-234.

9.Frankenberger R, Sindel J, Kramer N, Petschelt A. Dentin bond strength and marginal adaptation: direct composite resins vs ceramic inlays. Oper Dent 1999;24:147-155.

10.Giannini M, Carvalho RM, Martins LR, Dias CT, Pashley DH. The influence of tubule density and area of solid dentin on bond strength of two adhesive systems to dentin. J Adhes Dent 2001;3:315-324.

11.Hahn P, Schaller H, Hafner P, Hellwig E. Effect of different luting procedures on the seating of ceramic inlays. J Oral Rehabil 2000;27:1-8.

12.Ikemura K, Endo K. Effect of adhesion of new polymerization initiator systems comprising 5-monosubstituted barbituric acids, aromatic sulfinate amides, and ter-butyl peroxymaleic acid in dental adhesive resin. J Appl Polym Sci 1999;72:1655-1668.

13.Inokoshi S, Willems G, Van Meerbeek B, Lambrechts P, Braem M, Vanherle G. Dual-cure luting composites: Part I: Filler particle distribution. J Oral Rehabil 1993;20:133-146.

14.Krejci I, Lutz F, Reimer M. Wear of CAD/CAM ceramic inlays: restorations, opposing cusps, and luting cements. Quintessence Int 1994;25:199-207.

15.Magne P, Douglas WH. Porcelain veneers: dentin bonding optimization and biomimetic recovery of the crown. Int J Prosthodont 1999;12:111-121.

16.McCabe JF, Rusby S. Dentine bonding--the effect of pre-curing the bonding resin. Br Dent J 1994;176:333-336.

17.Pashley DH. In vitro simulations of in vivo bonding conditions. Am J Dent 1991;4:237-240.

18.Peters AD, Meiers JC. Effect of polymerization mode of a dual-cured resin cement on time-dependent shear bond strength to porcelain. Am J Dent 1996;9:264-268.

19.Rueggeberg FA, Margeson DH. The effect of oxygen inhibition on an unfilled/filled composite system. J Dent Res 1990;69:1652-1658.

20.Rueggeberg FA, Caughman WF. The influence of light exposure on polymerization of dual-cure resin cements. Oper Dent 1993;18:48-55.

21.Ruyter IE. Unpolymerized surface layers on sealants. Acta Odontol Scand 1981;39:27-32.

22.Sanares AM, Itthagarun A, King NM, Tay FR, Pashley DH. Adverse surface interactions between one-bottle light-cured adhesives and chemical-cured composites. Dent Mater 2001;17:542-556.

23.Shinkai K, Suzuki S, Leinfelder KF, Katoh Y. Effect of gap dimension on wear resistance of luting agents. Am J Dent 1995;8:149-151.

24.Sjogren G, Molin M, van Dijken J, Bergman M. Ceramic inlays (Cerec) cemented with either a dual-cured or a chemically cured composite resin luting agent. A 2-year clinical study. Acta Odontol Scand 1995;53:325-330.

25.Suzuki S, Leinfelder KF, Shinkai K. Wear resistance of resin cements. Am J Dent 1995;8:83-87.

26.Swift EJ, Jr., Perdigao J, Heymann HO. Bonding to enamel and dentin: a brief history and state of the art, 1995. Quintessence Int 1995;26:95-110.

27.Swift EJ, Jr., May KN, Jr., Wilder AD, Jr. Effect of polymerization mode on bond strengths of resin adhesive/cement systems. J Prosthodont 1998;7:256-260.

28.Tanaka J, Ishikawa K, Yatani H, Yamashita A, Suzuki K. Correlation of dentin bond durability with water absorption of bonding layer. Dent Mater J 1999;18:11-18.

29.Tay FR, Carvalho R, Sano H, Pashley DH. Effect of smear layers on the bonding of a self-etching primer to dentin. J Adhes Dent 2000;2:99-116.

30.Van Meerbeek B, Vargas M, Inoue S, Yoshida Y, Perdigao J, Lambrechts P, et al. Microscopy investigations. Techniques, results, limitations. Am J Dent 2000;13:3D-18D.

31.Wang Y, Spencer P. Exploring the nature of acid-resistant hybrid layer with wet bonding. Oper Dent 2004;29:650-655.

32.Yamauchi J. Study of dental adhesive containning phosphoric acid methacrylate monomer. Japanese Journal of Dental Materials 1986;5:144-154.

Table 1. Manufacturers and compositions of dual-cured adhesive systems used

Product (code) (Manufacturer)	Composition (manufacturer provided) (Batch Number)	Manufacturer's Instructions and exceptions
All Bond 2 (AB2) (Bisco Inc.) 4thGeneration	*Primer A:* acetone; ethanol; Na-N-tolylglycine; glycidylmethacrylate (0500003574); *Primer B:* acetone; ethanol; biphenyl dimethacrylate (0500003579); *Pre-Bond Resin:* Bis-GMA, TEGDMA; benzoyl peroxide; BHT (0500004345).	Mix primers A and B. Apply 5 consecutive coats to dentin; Dry all surfaces for 5-6 seconds with an air syringe; Light-cure 20 seconds; Apply thin layer of Pre-Bond Resin immediately prior to cementation. Air thin. Do not light-cure.
Bond 1 (B1) (Pentron Corp.) 5thGeneration	*Activator:* Methacrylate monomers in Ethanol and/or Acetone, Benzoyl Peroxide, Acetone (128878). *Resin:* Mixture of PMGDM, a condensation product of PMDA and Glycerol, Dimethacrylate HEMA and TMPTMA in ethanol and/or acetone with photo initiator, amine accelerator and stabilizer, Pyromellitic Dianhydride (129121).	Mix one drop of *Bond1* Dual Cure Activator with 2 drops of *Bond1* Primer/Adhesive. Using a fully saturated brush tip each time, apply two coats of *Bond1* Primer/Adhesive to tooth within 10 seconds; Apply a gentle stream of air for a minimum of ten (10) seconds. Hold air syringe 1 inch from site, positioned so as not to disturb resin surface. (Avoid excess of *Bond1* Primer/Adhesive in internal line angles or point angles).

TEGDMA: triethylene glycol dimethacrylate; Bis-GMA: bisphenol A diglycidyl ether methacrylate; PMDA: pyromellitic dianhydride; PMGDM: pyromellitic glycerol dimethacrylate; BHP: butylated hydroxytoluene; TMPTMA: trimethylolpropane trimethacrylate; HEMA: 2 hydroxyethyl methacrylate; GPDM: glycerophosphoric acid dimethacrylate.

Table 2. Manufacturers and compositions of the dual-cured resin cements used

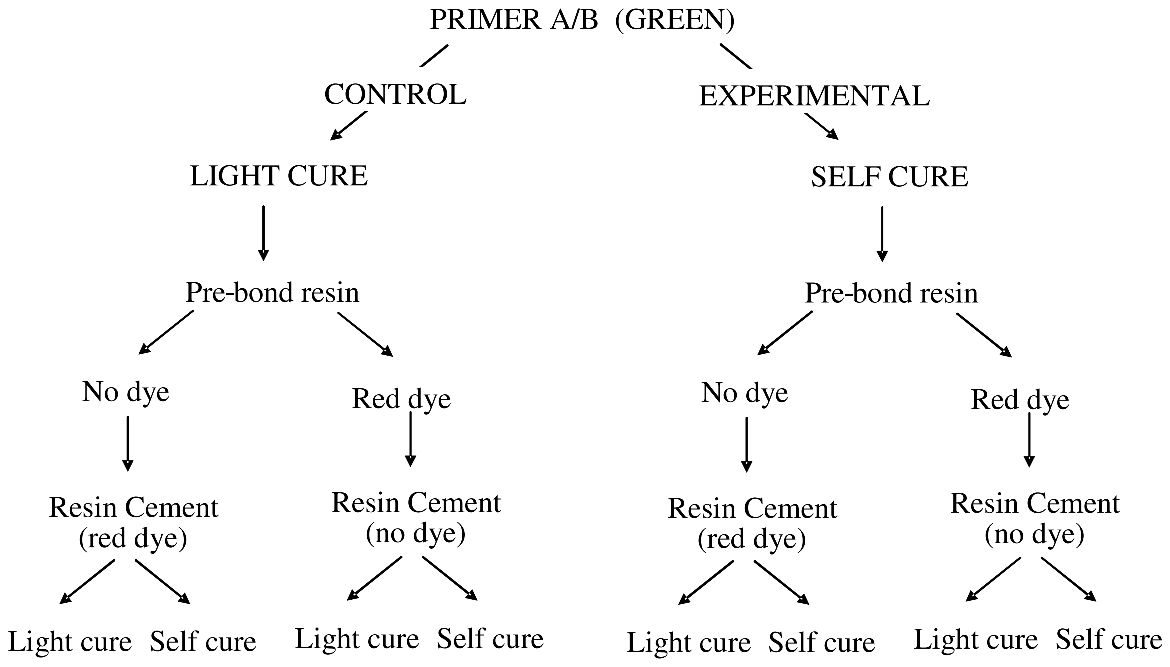
Product (Manufacturer)	Composition	Batch Number
Duolink (Bisco Inc.)	*Base:* Bis-GMA; TEGDMA; glass filler; urethane dimethacrylate. *Catalyst:* Bis-GMA; TEGDMA; glass filler.	0500003751
Lute-It! (Pentron Corp.)	In both Base & Catalyst: UDMA, HDDMA, Amine and inorganic pigments (in base only), Benzoyl Peroxide (in Catalyst only), UV Stabilizers (in both base and catalyst), Barium Glass, Inorganic Fluoride, Borosilicate Glass, Silane Silica Zirconia.	Base:130666 Catalyst:126388

TEGDMA: Triethylene glycol dimethacrylate, Bis-GMA: Bisphenol A diglycidyl ether methacrylate, UDMA: Urethane dimethacrylate, HDDMA: 1,6-hexanediol dimethacrylate.

Figure 1

ALL BOND 2

(4th Generation DBA)

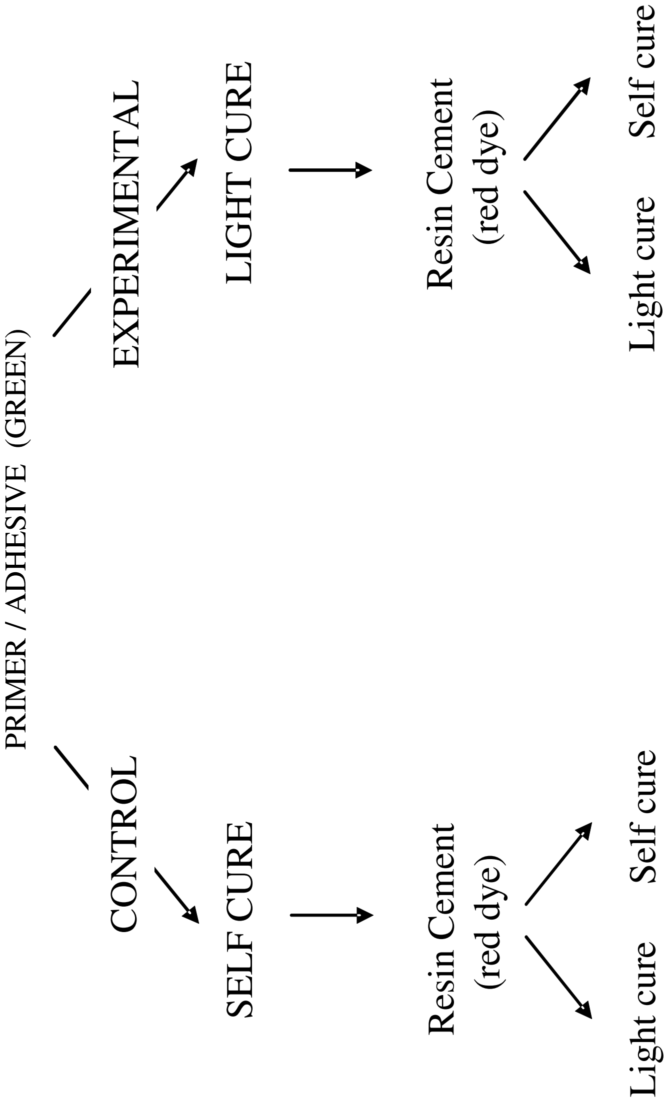


N = 5 per experimental group

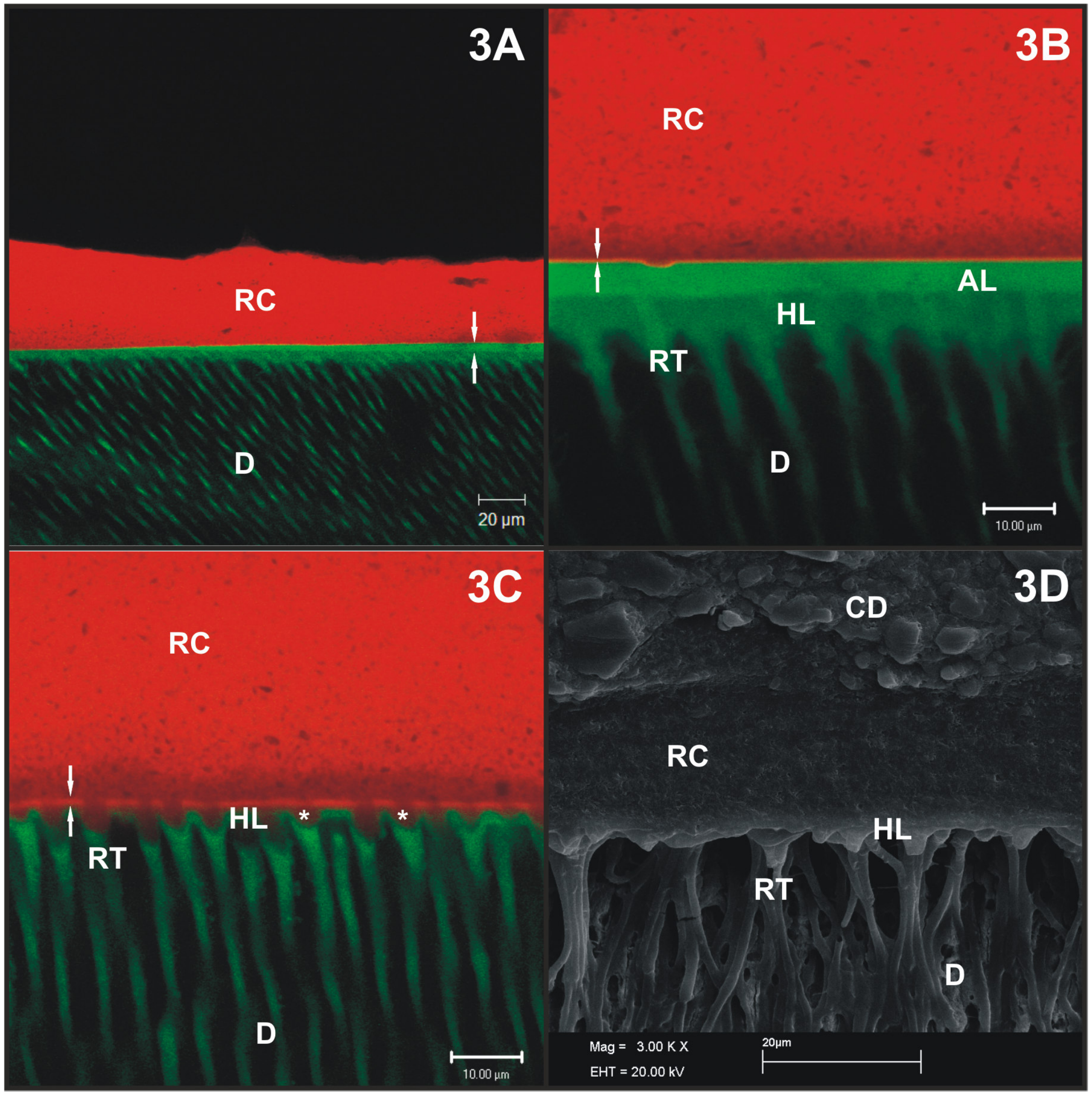
Figure 2

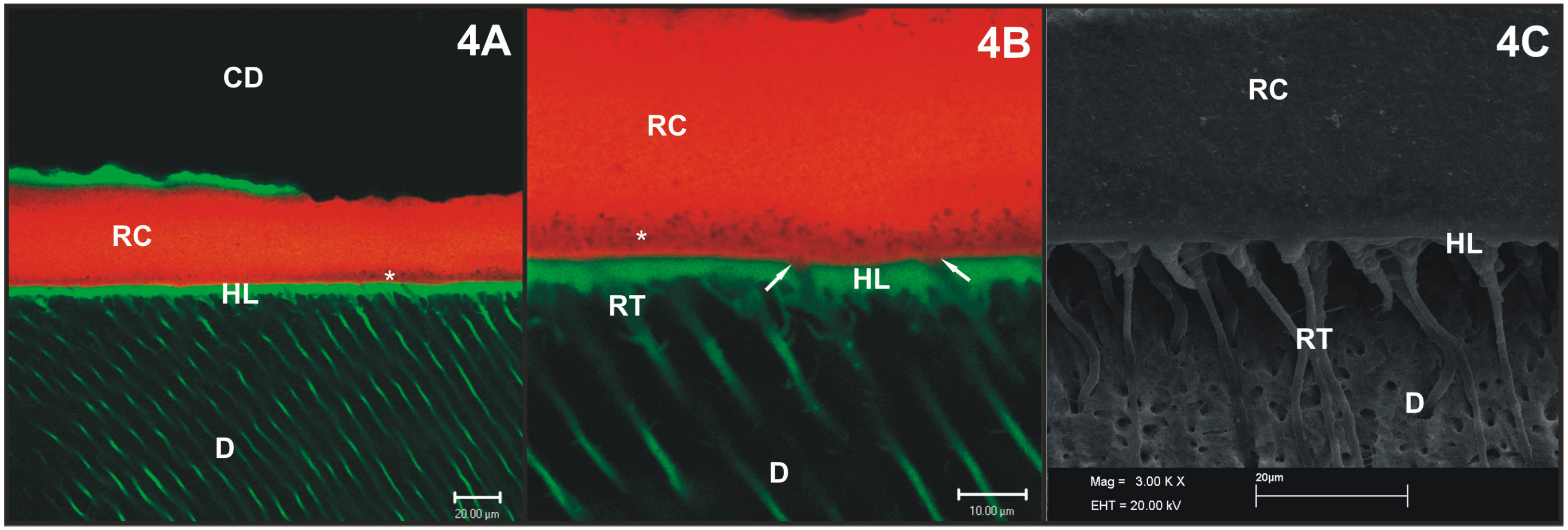
BOND 1

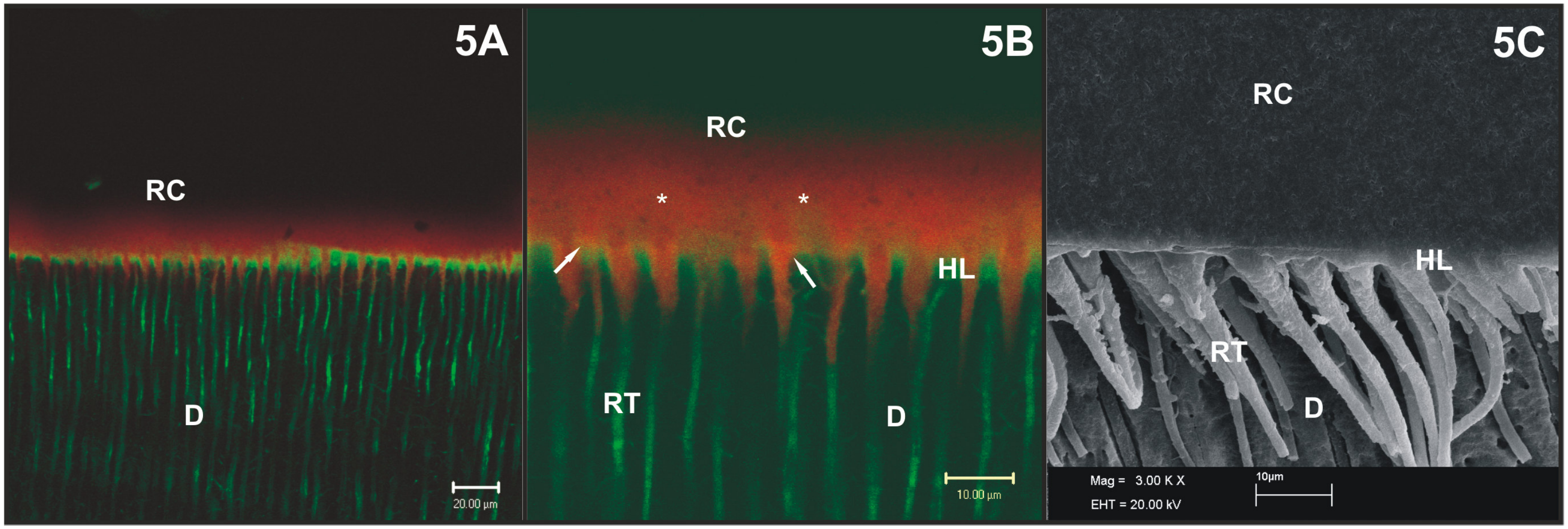
(5th Generation DBA)

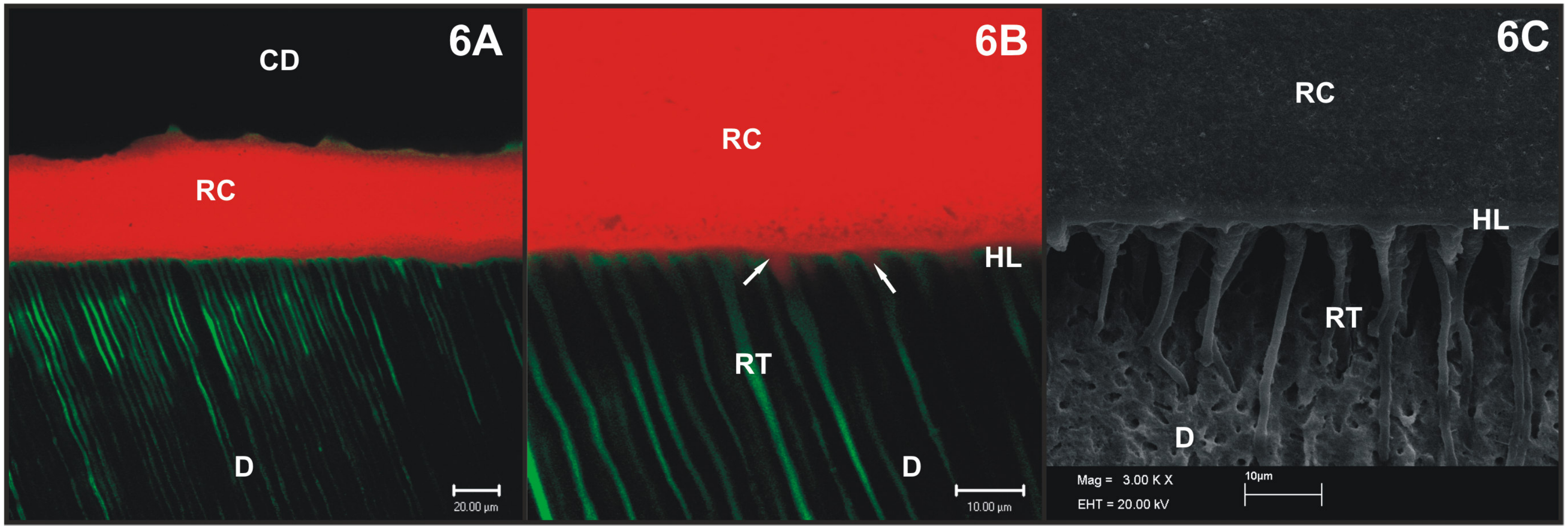


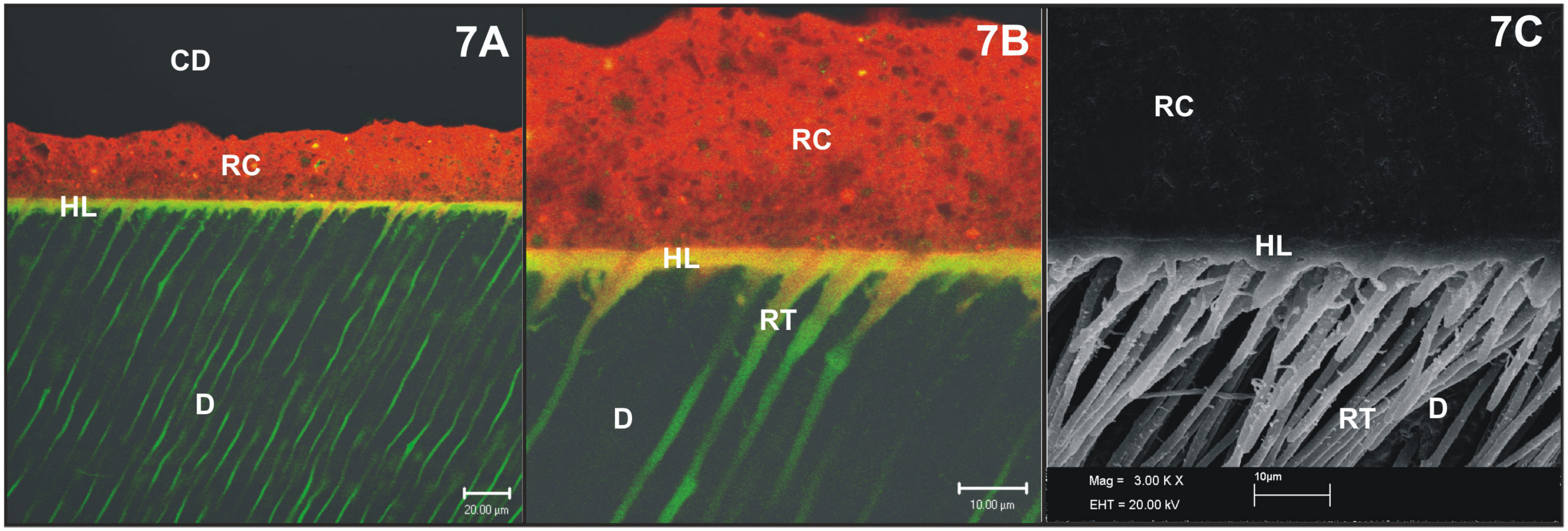
N = 5 per experimental group

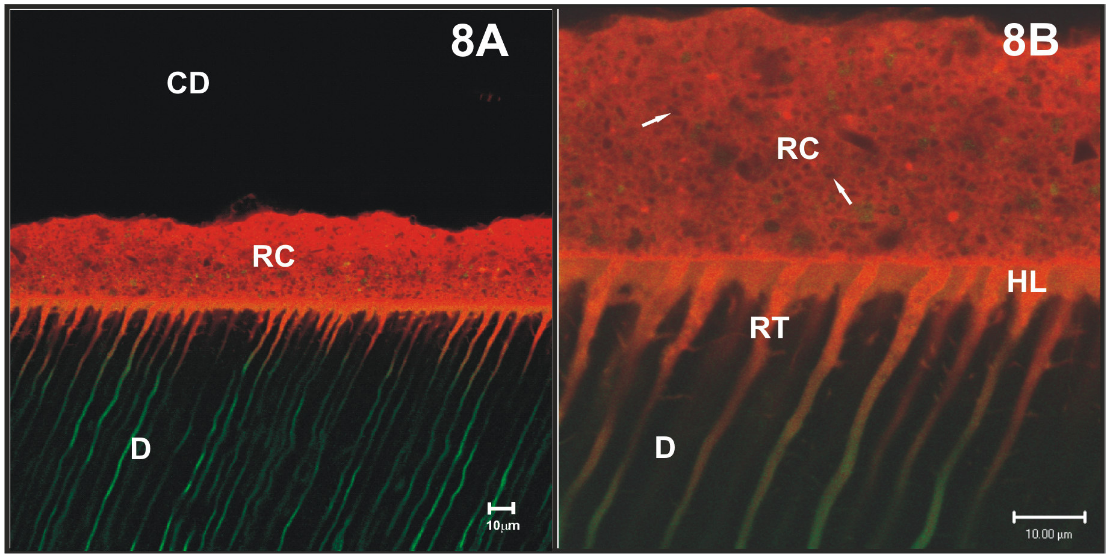

3A
RC
D
20 µm
3B
RC
AL
HL
RT
D
10.00 µm
3C
RC
HL
*
*
RT
D
10.00 µm
3D
CD
RC
HL
RT
D
Mag = 3.00 K X
EHT = 20.00 kV
20µm

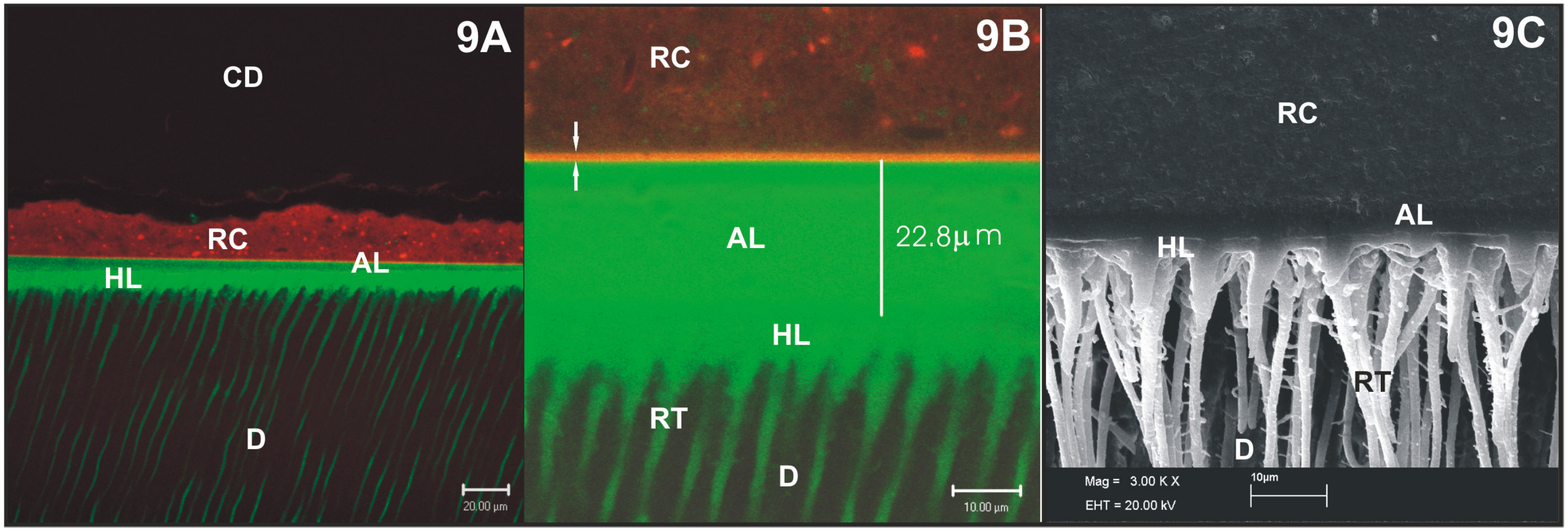

4A
CD
RC
HL
*
D
20.00 µm
4B
RC
*
HL
RT
D
10.00 µm
4C
RC
HL
RT
D
Mag = 3.00 K X
EHT = 20.00 kV
20µm

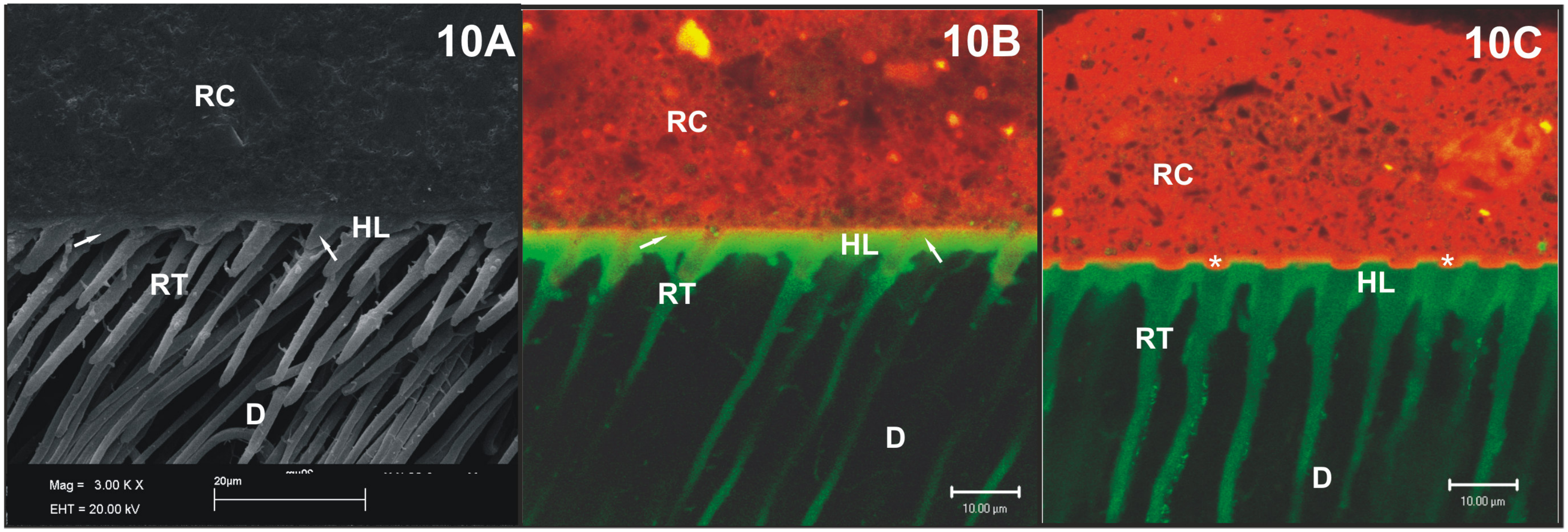

5A
RC
D
20.00 µm
5B
RC
* *
HL
RT
D
10.00 µm
5C
RC
HL
RT
D
Mag = 3.00 K X
EHT = 20.00 kV
10µm


6A
CD
RC
D
20.00 µm
6B
RC
HL
RT
D
10.00 µm
6C
RC
HL
RT
D
Mag = 3.00 K X
EHT = 20.00 kV
10µm


7A
CD
RC
HL
D
20.00 µm
7B
RC
HL
RT
D
10.00 µm
7C
RC
HL
RT
D
Mag = 3.00 K X
EHT = 20.00 kV
10µm


8A
CD
RC
D
10µm
8B
RC
HL
RT
D
10.00 µm


9A
CD
RC
HL
AL
D
20.00 µm
9B
RC
AL
22.8µm
HL
RT
D
10.00 µm
9C
RC
AL
HL
RT
D
Mag = 3.00 K X
EHT = 20.00 kV
10µm


10A
RC
HL
RT
D
Mag = 3.00 K X
EHT = 20.00 kV
20µm
10B
RC
HL
RT
D
10.00 µm
10C
RC
*
*
HL
RT
D
10.00 µm

LEGENDS:

Fig 1. Schematic diagram exhibiting the experimental groups created according to the curing modes of the adhesive layer and resin cement for All Bond 2 / Duolink.

Fig 2. Schematic diagram exhibiting the experimental groups created according to the curing modes of the adhesive layer and resin cement for Bond 1 / Lute-it.

Fig 3. Bonded interface created when All Bond 2 / Duolink was applied to the dentin surface and the primer (green) and the resin cement were light-activated as recommended by the manufacturer (control). (A) Representative CLSM image exhibiting a non-uniform primer layer (arrows). (B) The presence of a primer layer (AL) and the mixture between oxygen-inhibited uncured primer and resin cement components were noted (between arrows). (C) No primer layer was observed in some regions, which showed the resin cement penetration at the entrance of dentin tubules (asterisks) and a red line corresponding to the deposition of organic matrix from the resin cement (between arrows). (D) Representative SEM image of the bonded interface. RC – resin cement; HL – hybrid layer; RT – resin tag; D – dentin; AL – adhesive layer; CD – composite disc.

Fig 4. Bonded interface created when All Bond 2 / Duolink was applied to the dentin surface and the primer (green) was left in the uncured state (experimental group) and the resin cement (red) was light-activated. (A) A uniform hybrid layer and a dark red layer (asterisk) were noted along the whole extension of the dentin surface. The green shade above the resin cement corresponds to the primer AB, which was applied to the resin disc surface according to the manufacturer’s instructions. (B) Superficial resin cement penetration (arrows) was noted at the entrance of the dentin tubules, and a dark red layer (asterisk) corresponding to the presence of Pre Bond resin was observed within the resin cement layer (RC). (C) Representative SEM image of the bonded interface. HL – hybrid layer; RT – resin tag; D – dentin; CD – composite disc.

Fig 5. Bonded interface created when All Bond 2 / Duolink was applied to the dentin surface and the primer (green) was left in the uncured state (experimental) and the resin cement was allowed to light-cure for 40 s, but Rodhamine was incorporated to Pre-Bond resin (red) instead of in the resin cement (RC). (A) Pre-Bond resin penetration (red) into the dentin tubules and at the top of the hybrid layer was noted throughout the length of the dentin surface. (B) Orange areas indicating the mixture between Pre-Bond resin (red) and the primer (green) within the hybrid layer (arrows) and the mixture between Pre-Bond resin and resin cement (darker red areas, asterisks) were noted more clearly at higher magnification. (C) Representative SEM image showing corresponding areas of the bonded interface. RC – resin cement, HL – hybrid layer; RT – resin tag; D – dentin.

Fig 6. Bonded interface created when All Bond 2 / Duolink was applied to the dentin surface. The mixture of primers A and B (green) was left in the uncured state (experimental) and the resin cement (red) was allowed to self-cure. (A) The penetration of the resin cement components (red) was noted at the entrance of dentin tubules along the whole extension of the bonded interface. (B) Deeper resin cement penetration (red, arrows) at the entrance of the dentin tubules was observed when compared to the resin cement penetration observed when the resin cement was light-activated (Fig 4B). (C) Representative SEM image showing the bonded interface. RC – resin cement layer; HL – hybrid layer; RT – resin tag; D – dentin; CD – composite disc.

Fig 7. Bonded interface created when Bond 1 / Lute-it was applied to the dentin surface, the bonding agent (green) was left in the uncured state and the resin cement was light-activated: manufacturer's recommended directions (control). (A) Resin cement (red) penetration was observed into the entrance of all dentin tubules. A change in shade from green to yellow within the hybrid layer is seen denoting mixture between resin cement components (red) and bonding agent (green) along the whole bonded interface. (B) Higher magnification showing the resin cement (red) penetration into the dentin tubules and within the hybrid layer. (C) Representative SEM image of the bonded interface. RC – resin cement; HL – hybrid layer; RT – resin tag; D – dentin; CD – composite disc.

Fig 8. Bonded interface created when Bond 1 / Lute-it was applied to the dentin surface, the bonding agent was left in the uncured state (control) and the resin cement was allowed to self-cure. (A) Intense resin cement penetration (red) was observed into all dentin tubules and within the hybrid layer along the entire bonded interface. (B) Higher magnification showing the change in shade from green to red within the hybrid layer denoting the higher concentration of resin cement components within the hybrid layer. The distribution of filler particles (dark areas, arrows) was also noted within the resin cement layer, but none were present in the hybrid layer. RC – resin cement; HL – hybrid layer; RT – resin tag; D – dentin; CD – composite disc.

Fig 9. Bonded interface created in the 5th generation product when Bond 1 / Lute-it was applied to the dentin surface and bonding agent and resin cement were light-activated separately (experimental). (A) A non-uniform adhesive layer (green) and a 9-µm thick hybrid layer (green) were observed along the entire bonded interface. (B) A thick hybrid layer (green) and a yellow/orange line denoting the mixture between uncured, air-inhibited dentin bonding layer (AL) and resin cement (between arrows) were noted. (C) Representative SEM image of the bonded interface. HL – hybrid layer; RT – resin tag; RC – resin cement; D – dentin; AL – air-inhibited layer; CD – composite disc

Fig 10. Bonded interface created when Bond 1 / Lute-it was applied to the dentin surface and bonding agent (green) and resin cement (red) were light-activated separately. (A) Representative SEM image of the bonded interface. (B) No adhesive layers were observed at some regions of the bonded interface when the bonding agent was light-activated and resin cement penetration (red) into the dentin tubules (arrows) in those regions. (C) Resin cement penetration was also observed into the demineralized dentin (yellow-orange area, asterisks). RC – resin cement; HL – hybrid layer; RT – resin tag; D – dentin.

Effect of Curing Mode on the Polymerization Characteristics of Dual-Cured Resin Cement Systems

Cesar A.G. Arrais[a]/Marcelo Giannini[b]/Jennifer L. Waller[c]/ Mario F. de Goes[d]/
Frederick A. Rueggeberg[e]

[a] PhD candidate, Department of Restorative Dentistry, Piracicaba School of Dentistry, University of Campinas, Sao Paulo, Brazil.

[b] Associate Professor, Department of Restorative Dentistry, Piracicaba School of Dentistry, University of Campinas, Sao Paulo, Brazil.

[c] Associate Professor, Department of Biostatistics, Medical College of Georgia, Augusta, Georgia, USA.

[d] Associate Professor, Department of Restorative Dentistry, Dental Materials Section, Piracicaba School of Dentistry, University of Campinas, Sao Paulo, Brazil.

[e] Professor and Section Director, Department of Dental Materials, School of Dentistry, Medical College of Georgia, Augusta, Georgia, USA.

Corresponding author:
Corresponding author: Marcelo Giannini
Department of Restorative Dentistry/Operative Dentistry
Piracicaba School of Dentistry, UNICAMP
Av. Limeira, #901, Piracicaba, SP, 13414-900– Brazil
Telephone: 55 1934125340
Fax: 55 1934125218
E-mail: giannini@fop.unicamp.br

Key words: degree of conversion**,** dual-cured cementing systems, indirect restorations, self-cure.

ABSTRACT

Purpose: To evaluate the effects of different curing conditions on the degree of conversion (DC) of dual-cured cementing systems [combination of bonding agent (BA) and resin cement (RC)] using infrared spectroscopy.

Materials and Methods: Seven dual-cured BA/five RCs were used. The 4th generation products [Scotchbond Multipurpose Plus/RelyX (3M ESPE), Optibond/Nexus2 (Kerr), All Bond2/Duolink (Bisco), and Bond-It/Lute-It (Pentron)], and 5th generation materials [Bond1/Lute-It (Pentron), Prime&Bond NT Dual-Cure/Calibra (Dentsply), and Optibond Solo/Nexus 2 (Kerr)] were applied to surface of a horizontal attenuated-total-reflectance unit, and were polymerized using one of four conditions: self-cure (SC), direct light exposure (DLE/XL3000/3M) through glass slide or through pre-cured resin discs (shades A2;A4/2mm-thick/Z250/3M-ESPE). Infrared spectra were obtained after placing components (uncured), 5 and 10 min later (cured) (16 scans at $2 cm^{-1}$, FTS-40/Digilab/Bio-Rad). DC was calculated using standard techniques of observing changes in aliphatic-to-aromatic peak ratios pre- and post-curing. Data (n=5) were analyzed by two-way repeated measure ANOVA and Tukey's test ($p=0.05$). Spectral irradiance (mW/cm^2) of light passing through the glass slide or A2/A4 discs was measured (DAS-2100/Labsphere).

Results: Changes in aliphatic-to-aromatic peak ratios before and after placing RC onto the BA demonstrated that a combined layer was created on the diamond surface. All products exhibited higher DC after 10 minutes than after 5 minutes. No significant difference in DC was observed among light-activated groups regardless of the resin disc shade for most 4th generation cementing systems. The SC groups exhibited lower DC than the DLE groups for both 4th and 5th generation products.

Conclusion: The chemistry of the bonding interface changed when RCs were applied to uncured BAs. The presence of indirect restoration can decrease the DC of some cementing systems and the self-curing mode is less effective than light-activating one.

INTRODUCTION

The clinical success of composite and ceramic indirect restorations is attributed to the reliable bond between adhesive cementing systems (resin cements / bonding agents) and mineralized dental tissues.[12,23] Light intensity reaching the resin cement is strongly attenuated by either the distance from the light source or by the absorbing characteristics of the indirect restorative material. This attenuation results in low degree of conversion (DC) and compromised mechanical properties of the dentin/adhesive interface when only light-cured resin materials are used to bond the restorations.[21,24] In an attempt to overcome this problem, manufacturers developed dual-cured resin materials, which contain self-curing components to initiate the polymerization reaction in the absence of light.[14,15]

Dual-cured cementing systems contain a mixture of monomers and catalysts, and are formulated to not depend only on light activation to polymerize. Therefore, light activation of adhesive resins prior to delivering an indirect restoration might not be necessary. Among commercial resin-based indirect cementing systems available, manufacturer instructions differ widely in advocating the pre-curing of the dentin bonding agent (DBA). Some products advocate light-curing of the DBA prior to cementation, others indicate the clinician can choose to light cure or not, while others state that light curing should not be performed prior to resin cement application. Clinically, however, it would be an advantage not to light-cure the DBA separately. If the polymerized DBA thickness is large, its added dimensions would result in incomplete seating of the restoration, generating large marginal discrepancies and the necessity to adjust occlusion.[6]

It has been reported that acidic resin monomers from two-step total etch and self-etching adhesives may impair the polymerization of dual-cured cements and composites that are initiated via peroxide-amine binary redox catalysts.[26,28] As a consequence, low bond strength values are reported when light activation of the dentin bonding agent is not performed.[7,22] In order to overcome this chemical incompatibility, chemical co-initiators have been introduced, such as aryl sulfinic acid salts, organoboron compounds, and barbituric acid/cupric chloride.[11] These components react with the acidic resin monomers to produce either phenyl or benzenesulfonyl free radicals that initiate the reaction of dual-cured resin cements when light from the curing unit is not available.[11,27]

Several studies have demonstrated that ceramic or resin-based composite inlays/onlays reduce the amount of light reaching the bottom of the restoration, and therefore compromise photo-activation of photo-active luting materials.[2,3] Moreover, when evaluating *in vitro* occlusal wear, quantity of remaining double bonds, and cement system hardness, some authors indicate that the chemical curing mechanism alone is less effective than the light activated reaction when dual-cured resin cements were used.[2,8] However, there is no information regarding the DC of such dual-cured resin cements when they were combined with dual-cured adhesive systems in simulated clinical conditions when light intensity is strongly attenuated or totally absent.

Thus, the purpose of this study was to measure the DC of representative commercial 4th and 5th generation dual-cured cementing systems when they were light-activated with little attenuation (through a microscope slide) or when light was attenuated by passing through pre-cured resin discs (shades A2/A4), or when light from the curing unit was totally absent. The research hypotheses were: (1) within a given dual-cured cementing system, conversion using direct light-cure (low light attenuation) will be higher than when the systems were allowed to self-cure only; (2) The attenuation of curing light to the dual-cured cementing system by passing through pre-cured resin discs will result in lower DC of all systems when compared to when light passed through only a glass slide (low attenuation); (3) for similar thickness of pre-cured composite, the conversion of dual-cured cementing systems when light-cured would be less for the darker-shaded composite; and (4) DC after 10 min will be higher than that measured after 5 min from polymerization initiation for both SC and light-curing modes.

MATERIALS AND METHODS

Degree of Conversion

Four 4th and three 5th generation adhesive systems (Tables 1 and 2) and their recommended dual-cured resin cements (Table 3) were used (adhesive system / resin cement): All Bond2 / Duolink (AB2/DUO; Bisco), Bond-It / Lute-It (BIT/LUTE; Pentron), Optibond / Nexus 2 (OPT/Nexus; Kerr), Scotchbond Multipurpose Plus / Rely X (SBMP/RelyX; 3M ESPE); Bond1 / Lute-It (B1/LUTE; Pentron); Prime & Bond NT Dual-Cure / Calibra (NTD/Cal; Dentsply) and Optibond Solo Dual Cure / Nexus 2 (SOLOD/Nexus, Kerr), respectfully. Light-cured composite resin discs (2-mm thick ,10 mm in diameter – A2/A4 shade – Z250, lot# 5LB; 3M ESPE) were prepared to simulate overlying laboratory-processed composite resin restorations. The adhesive systems and resin cements were applied as described on Tables 1 and 2 to a horizontal diamond ATR element (Golden Gate, Specac, Woodstock, GA, USA) in the optical bench of a Fourier transform infrared spectrometer (FTIR) (FTS-40, Digilab/BioRad, Cambridge, MA, USA). All adhesive systems were placed according to manufacturer instructions, but none were light-cured prior to placement of the resin cement. Adhesive tape (3M) was placed around the diamond surface to act as spacer, ensuring standard thickness for all specimens (100 – 120 µm). The deposited material was covered with Mylar strip and polymerized using 4 different curing modes: light activation (XL3000, sn#202149, power density: 600 mW/cm^2; 3M/ESPE) according to manufacturers' instructions through a glass slide (1 mm thick) (direct light curing (DLC)); light activation through A2 or A4-shade pre-cured resin discs (A2/A4); or they were allowed to self-cure under Mylar strip and the glass slide (SC), with no curing light exposure.

Monomer Conversion

Infrared spectra were collected between 1680 and 1500 cm^{-1} at a rate of one-per-second at 2-cm^{-1} resolution, from the moment when the first layer of adhesive resin was applied to the ATR surface through the next 10 min. Five replications were made for each test condition. The first scan collected following detection of the presence of the resin cement at the adhesive-covered diamond surface (as noted by a change in aliphatic-to-aromatic C=C absorption ratios – Fig 1) served to supply the infrared spectra of the uncured mixed resin (adhesive resin / resin cement) interface. Monomer conversion was calculated by standard methods using changes in the ratios of aliphatic-to-aromatic C=C absorption peaks in the uncured and cured states obtained from the infrared spectra.[18,20] The DC of all curing modes was compared within each product at 5 and 10 minutes from the time the resin cement was applied to the adhesive system, as well as between the two periods. All specimens were carefully removed from the FTIR spectrometer and measured for thickness to the nearest 0.01 mm using a digital micrometer (Series 406; Mitutoyo America Corp., Aurora, IL, USA) to ensure that pressure applied to either the microscope slide of pre-polymerized resin disc provided the same thickness for all specimens.

Light irradiance values

The irradiance (mW/cm^2) of the curing unit was determined using a laboratory-grade spectral radiometer (DAS 2100, Labsphere, N. Sutton, NH, USA) with a 7.62 cm-diameter integrating sphere. Five measurements were obtained when the glass slide or the A2/A4 pre-cured resin discs were placed between the integrating sphere aperture and the light guide tip. Irradiance values were obtained between 350 and 600 nm by dividing the total emitted power (mW) by the area of the sphere aperture.

Statistical Analyses

A two-way repeated measure analysis of variance (ANOVA) (effect of curing mode and time) was performed for each product when the DC was the variable selected, and one-way ANOVA was performed to compare the differences in light intensity.

All statistical tests were performed at a pre-set alpha of 0.05 and followed by Tukey’s post-hoc test.

RESULTS

Monomer Conversion - Within dual-cured cementing systems

For most dual-cured cementing systems, a decrease in aliphatic-to-aromatic C=C absorption ratios was noted when the dual-cured resin cements were applied to the diamond surface containing uncured bonding agents (Fig 1). The only exception was observed for SOLOD, which showed an increase in the C=C absorption ratio when the resin cement was applied.

Table 4 displays DC results of all 4th and 5th generation dual-cured cementing systems, respectively. No significant differences in the DC were observed when A2 values were compared to DLC for the 4th generation cementing systems, except for OPT/Nexus at 5 min. However, with the 5th generation systems, the A2 groups exhibited lower DC than the DLC groups (Table 4). The DC of A4 specimens was significantly lower than that of the DLC group in most of the dual-cured cementing systems. The only exception was when AB2/DUO, BIT/LUTE (at 5 min) and SBMP/Rx were used, which showed no significant differences in DC between DLC and A4 groups.

For most of the 4th and 5th dual-cured cementing systems, the SC group exhibited lower DC than DLC, A2 and A4 experimental groups. The only exceptions were observed for BIT/LUTE at 10 min, which showed no significant differences among SC, A2 and A4 groups, and for B1/LUTE and SOLOD/Nexus, which showed no significant differences between SC and A4 groups at 10 min. The thickness of all specimens ranged from 100 µm to 120 µm.

Monomer Conversion - Within curing modes

All 4th and 5th generation cementing systems exhibited lower DC at 5 min than at 10 min in all curing modes. The only exception was seen in DLC of BIT/LUTE where no difference in DC values was found between 5 and 10 min (Tables 4).

Light attenuation of pre-cured resin discs

Table 5 presents irradiance values measured when light passed through the microscope glass slide, as well as through A2- and A4-shade pre-cured resin discs. When the A2-shade pre-cured resin disc was used, irradiance decreased approximately 89%, while 92% lower irradiance was noted when using the A4 disc.

DISCUSSION

The results of this study demonstrated that all research hypotheses tested were accepted or rejected depending on the curing mode and the dual-cured cementing system generation evaluated. The research hypothesis stating that conversion using direct light-cure would be higher than when the systems were allowed to self-cure within the same dual-cured cementing system was accepted for both cementing system generations, at 5 and 10 min. This finding agrees with other reports, which showed that the self-curing mode was less effective when compared to the dual-cured or photo-cured ones.[2,8] One possible explanation for this finding may be related to the slow rate of polymerization promoted by the self-curing mode, as was confirmed when low DC was observed at five min in all products when they were allowed to self-cure (Table 4). Rueggeberg and Caughman[17] speculated that the change in viscosity due to the reaction of polymerization caused the inability of radicals to migrate and the final conversion is impaired as consequence. Further studies are necessary to compare the DC promoted by the SC mode with that obtained with DLC mode after 24 h.

When compared to the power density obtained when using the glass slide, only 11% and 8% of the total irradiance reached the cementing systems when pre-cured A2 and A4 -shade resin discs were used, respectively (Table 5). However, even when light intensity decreased approximately 92%, no difference in DC was observed for most of the 4th generation cementing systems when compared to the values of DLC groups after 10 min. Therefore, the research hypothesis stating that the presence of pre-cured resin disc may affect the DC was invalidated for the 4th generation dual-cured cementing systems evaluated after 10 min. Considering the fact that the main feature of such cementing systems is the presence of benzoyl peroxide not only in the resin cements, but also in the adhesive systems, the composition of the mixture obtained from resin cements and adhesive systems has higher content of self-curing components than that of these materials when they are not mixed together. As the higher content of such self-curing components affect the DC of self-cured polymer materials,[1] the higher amine/benzoyl peroxide content may have ensured that differences in light intensity did not affect the DC of the cementing systems.

On the other hand, all 5th generation dual-cured cementing systems exhibited lower DC when pre-cured resin discs were used, so the same research hypothesis discussed above was confirmed for the 5th generation systems. Differently from the 4th generation cementing systems, the 5th generation dual-cured cementing systems have benzoyl peroxide only in the resin cements and parabenzene sulfinic acid sodium salts in the adhesive systems. These aryl sulfinic acid salts are used to reduce or even eliminate the incompatibility between the acidic monomers from the adhesive systems and the tertiary aromatic amines from the resin cements.[11,26] Therefore, the lower content of self-curing components in the 5th generation systems may have not been capable of compensating for the decrease in light intensity promoted by the presence of pre-cured resin discs.

Among all 5th generation adhesive systems evaluated, Bond 1 was the only adhesive system having benzoyl peroxide instead of aryl sulfinic acid salts in its composition. However, the DC of this dual-cured cementing system was also affected by the presence of the pre-cured resin discs. One possible explanation for this finding may be related to the lack of the aryl sulfinic acid salts in its composition. Although the amount of benzoyl peroxide was increased due to its presence in both the resin cement and adhesive system, it is possible to speculate that the chemical incompatibility between the adhesive resin and dual-cured resin cement may have impaired the formation of starting radicals and consequently the self-curing reaction was compromised.[19,22] Thus, the polymerization may rely most on light exposure, which was drastically reduced by the presence of pre-cured resin discs. This speculation might also explain the lower DC of A4 experimental group when compared with that of A2 when B1/LUTE was used. Despite the lower light intensity observed when the A4-shade pre-cured resin disc was used (Table5), B1/LUTE was the only cementing system showing significant differences in DC when values of A2 and A4 groups were compared to each other. However, the effects of self-curing mechanisms in compensating light attenuation can only be confirmed when comparing the DC of light-activated and dual-cured adhesive systems applied together with dual-cured resin cements.

This study compared DC at 5 and 10 minutes after initial mixture of components. Most manufacturers recommend the clinician wait at least five minutes prior to adjusting a recently cemented indirect restoration. All dual-cured cementing systems exhibited lower DC after 5 min than the values observed after 10 min within A2, A4 and SC experimental groups. Thus, the research hypothesis that the cementing systems would show higher DC at 10 min than at 5 min was confirmed. When light was not available, the difference in DC between 5 and 10 minute intervals ranged approximately from 4% to 17% (Table 4). As a consequence, mechanical properties such as flexural and compressive strengths, elastic moduli, and hardness may be proportionally affected by this range in the DC.[5,13] Therefore, longer time period should pass before performing occlusal adjustment or removing excess marginal resin cement than is currently advocated (5 minutes).

The results of this study need to be considered with respect to many aspects related to testing conditions. The penetration of the infrared beam into the materials placed above the crystal was approximately 3 microns. Thus, changes in resin content upon introducing the uncured cement paste into the unpolymerized dentin bonding agent were only observed within this thickness. However, the area of infrared observation, and thus characterization of conversion, is considered to be clinically relevant, as it is similar to that of a hybrid layer that would be present on acid etched dentin. Also, some of the dentin bonding agents used in this study are acidic in nature.[22] It has been demonstrated that the acidity of self-etching adhesive systems is neutralized after placement by the dissolution of the hydroxyapatate dentin matrix.[10] Such neutralization is thought to permit maximal conversion, as opposed to when curing takes place at low pH values.[28] The ATR plate upon which the acidic bonding agents were placed could not provide any buffering capability to the dentin bonding agents, and thus could not truly simulate the clinical situation. For this reason, no self-etching adhesive systems were evaluated in this study. As 4th and 5th generation adhesive systems are applied to demineralized dentin, which does not have hydroxyapatite, no change in pH is expected in the clinical situation, considering the evidences that the resin monomers do not fully infiltrate the demineralized dentin and therefore do not react with hydroxyapatite.[9,25] Thus, the experimental system used seems to not be different from the *in vivo* condition when applying acidic bonding agents to dentin.

This *in vitro* study was based on well-controlled laboratory conditions. However, other variables such as presence of water and quality of resin infiltration into demineralized dentin can affect the DC and the mechanical properties of polymer materials when they are applied to teeth.[4,16] The monomer conversion values for dentin bonding agents applied and light cured alone were not determined in this study. Because the chemistry of the analyzed interface changed when the resin cement was applied and diffused into the uncured bonding agent, direct comparison of conversion values between the light cured bonding agent alone and that of the mixture of bonding agent and cement cannot be made. Thus, the significance of these differences is not known. Only additional testing, such as bond strength comparison between specimens of similar curing modes, would reveal the importance of such changes.

CONCLUSION

Within the limitations of this study, the following conclusions were made: (1) monomer conversion using direct light exposure was higher than when the systems were allowed to self-cure only; (2) The attenuation of curing light to the dual-cured cementing system by passing through pre-cured resin discs resulted in lower DC for the 5th generation cementing systems; (3) darker-shaded composite did not result in lower DC in all products; and (4) DC after 10 min was higher than that measured after 5 min from polymerization initiation for both SC and light-curing modes in almost all products.

Acknowledgments

The authors are indebted to Bisco Inc., Kerr Inc., Pentron Inc., Dentsply Caulk Inc. and 3M-ESPE Company for providing all restorative materials. This study was supported by CAPES Brazil (BEX0184/05-5) and FAPESP (03/03645-0) and the Medical College of Georgia School of Dentistry, Augusta, GA, USA.

Clinical Relevance

A combined layer created at the adhesive interface when dual-cured resin cements are placed on uncured bonding agents is capable of polymerizing even in the worst simulated clinical condition, in which light from the curing unit is strongly attenuated or totally absent.

REFERENCES:

1.Asmussen E. Setting time of composite restorative resins vs. content of amine, peroxide, and inhibitor. Acta Odontol Scand 1981;39:291-294.

2.Blackman R, Barghi N, Duke E. Influence of ceramic thickness on the polymerization of light-cured resin cement. J Prosthet Dent 1990;63:295-300.

3.Cardash HS, Baharav H, Pilo R, Ben-Amar A. The effect of porcelain color on the hardness of luting composite resin cement. J Prosthet Dent 1993;69:620-623.

4.De Munck J, Van Meerbeek B, Yoshida Y, Inoue S, Vargas M, Suzuki K, et al. Four-year water degradation of total-etch adhesives bonded to dentin. J Dent Res 2003;82:136-140.

5.Ferracane JL, Berge HX, Condon JR. In vitro aging of dental composites in water--effect of degree of conversion, filler volume, and filler/matrix coupling. J Biomed Mater Res 1998;42:465-472.

6.Frankenberger R, Sindel J, Kramer N, Petschelt A. Dentin bond strength and marginal adaptation: direct composite resins vs ceramic inlays. Oper Dent 1999;24:147-155.

7.Giannini M, De Goes MF, Nikaido T, Shimada Y, Tagami J. Influence of activation mode of dual-cured resin composite cores and low-viscosity composite liners on bond strength to dentin treated with self-etching adhesives. J Adhes Dent 2004;6:301-306.

8.Hasegawa EA, Boyer DB, Chan DC. Hardening of dual-cured cements under composite resin inlays. J Prosthet Dent 1991;66:187-192.

9.Hashimoto M, Ohno H, Kaga M, Sano H, Tay FR, Oguchi H, et al. Over-etching effects on micro-tensile bond strength and failure patterns for two dentin bonding systems. J Dent 2002;30:99-105.

10.Hume WR. Influence of dentine on the pulpward release of eugenol or acids from restorative materials. J Oral Rehabil 1994;21:469-473.

11.Ikemura K, Endo K. Effect of adhesion of new polymerization initiator systems comprising 5-monosubstituted barbituric acids, aromatic sulfinate amides, and ter-butyl peroxymaleic acid in dental adhesive resin. J Appl Polym Sci 1999;72:1655-1668.

12.Inokoshi S, Willems G, Van Meerbeek B, Lambrechts P, Braem M, Vanherle G. Dual-cure luting composites: Part I: Filler particle distribution. J Oral Rehabil 1993;20:133-146.

13.Lovell LG, Berchtold KA, Elliot JE, Lu H, Bowman CN. Understanding the Knetics and network formation of dimethacrylate dental resins. Polym Adv Technol 2001;12:335-345.

14.Milleding P, Ortengren U, Karlsson S. Ceramic inlay systems: some clinical aspects. J Oral Rehabil 1995;22:571-580.

15.Nathanson D. Etched porcelain restorations for improved esthetics, part II: Onlays. Compendium 1987;8:105-110.

16.Paul SJ, Leach M, Rueggeberg FA, Pashley DH. Effect of water content on the physical properties of model dentine primer and bonding resins. J Dent 1999;27:209-214.

17.Rueggeberg FA, Caughman WF. The influence of light exposure on polymerization of dual-cure resin cements. Oper Dent 1993;18:48-55.

18.Rueggeberg FA, Hashinger DT, Fairhurst CW. Calibration of FTIR conversion analysis of contemporary dental resin composites. Dent Mater 1990;6:241-249.

19.Ruyter IE. Unpolymerized surface layers on sealants. Acta Odontol Scand 1981;39:27-32.

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

21.Ruyter IE, Oysaed H. Conversion in denture base polymers. J Biomed Mater Res 1982;16:741-754.

22.Sanares AM, Itthagarun A, King NM, Tay FR, Pashley DH. Adverse surface interactions between one-bottle light-cured adhesives and chemical-cured composites. Dent Mater 2001;17:542-556.

23.Sjogren G, Molin M, van Dijken J, Bergman M. Ceramic inlays (Cerec) cemented with either a dual-cured or a chemically cured composite resin luting agent. A 2-year clinical study. Acta Odontol Scand 1995;53:325-330.

24.Strang R, McCrosson J, Muirhead GM, Richardson SA. The setting of visible-light-cured resins beneath etched porcelain veneers. Br Dent J 1987;163:149-151.

25.Tay FR, Gwinnett JA, Wei SH. Micromorphological spectrum of acid-conditioned dentin following the application of a water-based adhesive. Dent Mater 1998;14:329-338.

26.Tay FR, Suh BI, Pashley DH, Prati C, Chuang SF, Li F. Factors contributing to the incompatibility between simplified-step adhesives and self-cured or dual-cured composites. Part II. Single-bottle, total-etch adhesive. J Adhes Dent 2003;5:91-105.

27.Wang SF, Chuang CP, Lee WH. Free radical reaction of - allyl-sulfonylalkyl substituted aromatic derivatives. Tetrahedron 1999;55:6109-6118.

28.Yamauchi J. Study of dental adhesive containning phosphoric acid methacrylate monomer. Japanese Journal of Dental Materials 1986;5:144-154.

LEGENDS:

Figure 1 Illustrative FTIR spectrum exhibiting the changes in absorbing peak corresponding to C=C aromatic double bond (1608 and 1582) after resin cement application on the top of uncured bonding agent.

Table 1 Brand, composition, batch number and manufacturers' instructions of the 4^h generation dual-cured adhesive systems used

Product (code) (Manufacturer)	Composition (manufacturer supplied) (Batch Number)	Manufacturer's Instructions and exceptions
All Bond 2 (AB2) (Bisco Inc., Schaumburg, IL, USA)	*Primer A:* acetone; ethanol; Na-N-tolylglycine; glycidylmethacrylate (0500003574); *Primer B:* acetone; ethanol; biphenyl dimethacrylate (0500003579); *Pre-Bond Resin:* Bis-GMA, TEGDMA; benzoyl peroxide; BHT (0500004345).	Mix primers A and B. Apply 5 consecutive coats to dentin; Dry all surfaces for 5-6 seconds with an air syringe; Light-cure 20 seconds*; Apply thin layer of Pre-Bond Resin immediately prior to cementation. Air thin. Do not light-cure.
Bond-It! (BIT) (Pentron Corp., Wallingford, CT USA)	*Primer A:* NTG-GMA magnesium salt in acetone, Acetone (123280). *Primer B:* Mixture of PMGDM, a condensation product of PMDA and Glycerol (126514). *Unfilled dual resin activator:* Mixture of UDMA and HDDMA resins with self curing initiator, stabilizer, Benzoyl peroxide (110743). *VLC Adhesive*: Dental methacrylate resin mixture with photo initiator, amine, and stabilizer (128389).	Mix equal parts of primer A and B. Apply 5 coats to the etched surface to achieve a shiny appearance; Dry only after final coat. Mix equal parts of Bond-It Light cure resin and Dual-Cure Activator and apply; Surface may be light cured or allowed to self-cure.
Optibond (OPT) (Kerr Corp., Orange, CA, USA)	*Primer*: Ethyl Alcohol, Alkyl Dimethacrylate Resins, Water (423435). *Dual Cure Paste (3B)*: Uncured Methacrylate Ester Monomers; Triethylene Glycol Dimethacrylate (424560); Inert glass filler, pigment and stabilizers. *Dual Cure Activator Resin (3A):* Uncured Methacrylate; Ester Monomers; Benzoyl Peroxide (423073).	Apply Optibond Prime (bottle 1) to dentin and enamel surfaces with microbrush, scrubbing the surface for thirty (30) seconds; Air dry for 5 seconds; Dispense Optibond Dual Cure paste (3B) and 1 drop of Dual Cure Activator (3A) and thoughtfully mix them for 15 seconds; Apply a thin coat of the mixed dual cure to the dentin surface.; Do not air thin and do not light cure it.
Scotchbond Multipurpose (SBMP) (3M ESPE, St. Paul, MN, USA)	*Primer:* water; 2-hydroxyethyl methacrylate; copolymer of acrylic and itaconic acids (5AT). *Activator:* ethyl alcohol; sodium benzenesulfinate (5KT); *Catalyst:* Bis-GMA; 2-hydroxyethyl methacrylate; benzoyl peroxide (3AP).	Apply activator (1.5) to enamel and dentin. Dry gently for 5 seconds; apply primer (2.0) to enamel and dentin. Dry gently for 5 seconds; apply catalyst (3.5) to enamel and dentin; mix and apply a self-cure or dual-cure luting material to the bonding surface of the restoration; seat the restoration. If a dual-cure cement was used, light-cure the margins.

TEGDMA: Triethylene glycol dimethacrylate, Bis-GMA: Bisphenol A diglycidyl ether methacrylate, UDMA: Urethane dimethacrylate, PMDA: Pyromellitic Dianhydride; HADDMA: 1,6-hexanediol dimethacrylate; PMGDM: pyromellitic glycerol dimethacrylate; BHP: Butylated Hydroxytoluene

* The adhesive systems were not light-activated before the cementation of indirect resin composite disc.

Table 2 Brand, composition, batch number and manufacturers' instructions of the 5th generation dual-cured adhesive systems used

Product (Manufacturer)	Composition Manufacturer supplied) (Batch Number)	Manufacturer's Instructions and exceptions
B1 (Pentron Corp.)	*Activator:* Methacrylate monomers in Ethanol and/or Acetone, Benzoyl Peroxide Unknown, Acetone (128878). *Resin:* Mixture of PMGDM, a condensation product of PMDA and Glycerol, Dimethacrylate HEMA and TMPTMA in ethanol and/or acetone with photo initiator, amine accelerator & stabilizer, Pyromellitic Dianhydride (129121).	Mix one drop of *Bond1* Dual Cure Activator with 2 drops of *Bond1* Primer/Adhesive. Using a fully saturated brush tip each time, apply two coats of *Bond1* Primer/Adhesive to tooth within 10 seconds; Apply a gentle stream of air for a minimum of ten (10) seconds. Hold air syringe 1 inch from site, positioned so as not to disturb resin surface. (Avoid excess of *Bond1* Primer/Adhesive in internal line angles or point angles).
NTD (Dentsply Caulk, Milford, DE, USA)	*Resin:*Acetone, Urethane dimethacrylate resin, Dipentaerythritol pentaacrylate phosphate, Polymerizable dimethacrylate resins, Polymerizable trimethacrylate resins (050413). *Activator:* Aromatic Sodium Sulfinate, (Self cure initiator), Acetone, Ethanol (041110).	Place 1-2 drops of the adhesive and equal number of drops of Self-Cure Activator into a mixing well; Mix contents for 1-2 seconds with a clean, unused brush tip; Using the disposable brush supplied, immediately apply mixed adhesive/activator to thoroughly wet all the tooth surfaces. These surfaces should remain fully wet for 20 seconds and may necessitate additional applications of mixed adhesive/activator; Remove excess solvent by gently drying with a dental syringe for at least 5 seconds. Surface should have a uniform glossy appearance. Cure mixed adhesive/activator for 10 seconds using a curing light unit.*
SOLOD (Kerr Corp.)	*Adhesive resin:* Ethyl alcohol, Alkyl dimethacrylate resins, Barium aluminoborosilicate glass, Fumed silica (silicon dioxide), Sodium hexafluorosilicate (428904). *Activator:* Ethyl alcohol, Alkyl dimethacrylate resins, Benzene Sulfinic Acid, Sodium Salt (428260).	Dispense one drop of Optibond Solo Plus and Optibond Solo Activator into a disposable mixing well. Mix for 3s; apply mixture to dentin with a light brushing for 15s to cover dentin surface; lightly air thin for 3s; light-cure for 20s.*

PMDA: Pyromellitic dianhydride; PMGDM: pyromellitic glycerol dimethacrylate; BHP: Butylated hydroxytoluene; TMPTMA: Trimethylolpropane trimethacrylate; HEMA: 2-Hydroxyethyl methacrylate.

* The adhesive systems were not light-activated before the cementation of indirect resin composite disc.

Table 3 Brand, composition and batch number of the dual-cured resin cements used

Product (code) (Manufacturer)	Composition	Batch Number
Duolink (DUO) (Bisco Inc.)	*Base:* Bis-GMA; TEGDMA; glass filler; urethane dimethacrylate. *Catalyst:* Bis-GMA; TEGDMA; glass filler.	0500003751
Nexus 2 (Nexus) (Kerr Corp.)	*Activator:* ethyl alcohol; alkyl dimethacrylate resins; benzene sulfinic acid sodium salt. Monomers of methacrylic acid esters, Ba–Al –borosilicate glass, chemical and photoinitiators.	Base:423638 Cataly.:423975
Lute-It! (LUTE) (Pentron Corp.)	In both Base & Catalyst: UDMA, HDDMA, Amine and inorganic pigments (in base only), Benzoyl Peroxide (in Catalyst only), UV Stabilizers (in both base and catalyst), Barium Glass, Inorganic Fluoride*, Borosilicate Glass, Silane Silica Zirconia.	Base:130666 Cataly.:126388
Calibra (CAL) (Dentsply Caulk)	Base paste: Barium boron fluoroalumino silicate glass, Bis-GMA resin, Polymerizable dimethacrylate resin, Polymerizable dimethacrylate resin, Hydrophobic Amorphous Fumed Silica, Titanium Dioxide, Other colorants are inorganic iron oxides. Catalyst paste: Barium boron, fluoroalumino silicate glass, Bis-GMA resin, Polymerizable dimethacrylate resin, Hydrophobic Amorphous Fumed Silica, Titanium Dioxide, Benzoyl Peroxide.	Base:0504111 Cataly.:0505121
Rely X (Rx) (3M ESPE)	Paste A: Silane treated ceramic, Triethylene glycol dimethacrylate (tegdma), Bis-GMA, Silane treated silica, Functionalized dimethacrylate polymer, Paste B:_Silane treated ceramic, TEGDMA, Bis-GMA, Silane treated silica, Functionalized dimethacrylate polymer.	EYFH

TEGDMA: Triethylene glycol dimethacrylate, Bis-GMA: Bisphenol A diglycidyl ether methacrylate, UDMA: Urethane dimethacrylate, HDDMA: 1,6-hexanediol dimethacrylate.

Table 4 Degree of Conversion (%) (DC) for adhesive/resin cement systems (mean (SD))

Bonding agent / Cement	Time after mixing or exposure	DLC	A2	A4	SC
AB2/DUO	5 min	61.2 (0.8) Aa	58.6 (0.4) Aa	58.4 (1.2) Aa	37.1 (4.3) Ab
	10 min	63.4 (0.9) Ba	61.7 (0.6) Ba	61.5 (0.9) Ba	49.5 (1.0) Bb
Bit/LUTE	5 min	63.4 (1.2) Aa	58.5 (2.8) Aab	53.5 (3.2) Ab	45.7 (9.7) Ac
	10 min	66.3 (0.8) Aa	62.8 (2.0) Bab	59.3 (2.0) Bab	57.3 (3.2) Bb
OPT/Nexus	5 min	65.0 (0.3) Aa	62.2 (0.8) Ab	62.0 (0.6) Ab	39.5 (2.4) Ac
	10 min	66.8 (0.3) Ba	65.2 (0.5) Bab	64.7 (0.5) Bb	55.9 (0.7) Bc
SBMP/Rx	5 min	52.0 (2.5) Aa	50.1 (3.4) Aa	48.1 (1.1) Aa	36.2 (3.0) Ab
	10 min	55.1 (2.4) Ba	53.8 (3.1) Ba	52.6 (1.3) Ba	44.3 (2.4) Bb
B1/LUTE	5 min	59.3 (0.7) Aa	54.1 (0.5) Ab	52.3 (0.8) Ac	48.3 (0.7) Ad
	10 min	62.2 (0.9) Ba	58.3 (0.2) Bb	57.4 (0.7) Bbc	56.1 (0.9) Bc
NTD/Cal	5 min	59.0 (0.7) Aa	55.3 (1.1) Ab	54.6 (1.5) Ab	46.6 (2.2) Ac
	10 min	61.5 (0.9) Ba	58.1 (0.9) Bb	57.8 (0.9) Bb	52.6 (1.7) Bc
SoloD/Nexus	5 min	70.5 (1.9) Aa	66.6 (1.2) Ab	65.8 (1.8) Ab	61.1 (2.0) Ac
	10 min	72.6 (1.8) Ba	69.2 (1.2) Bb	68.8 (1.7) Bbc	65.8 (1.9) Bc

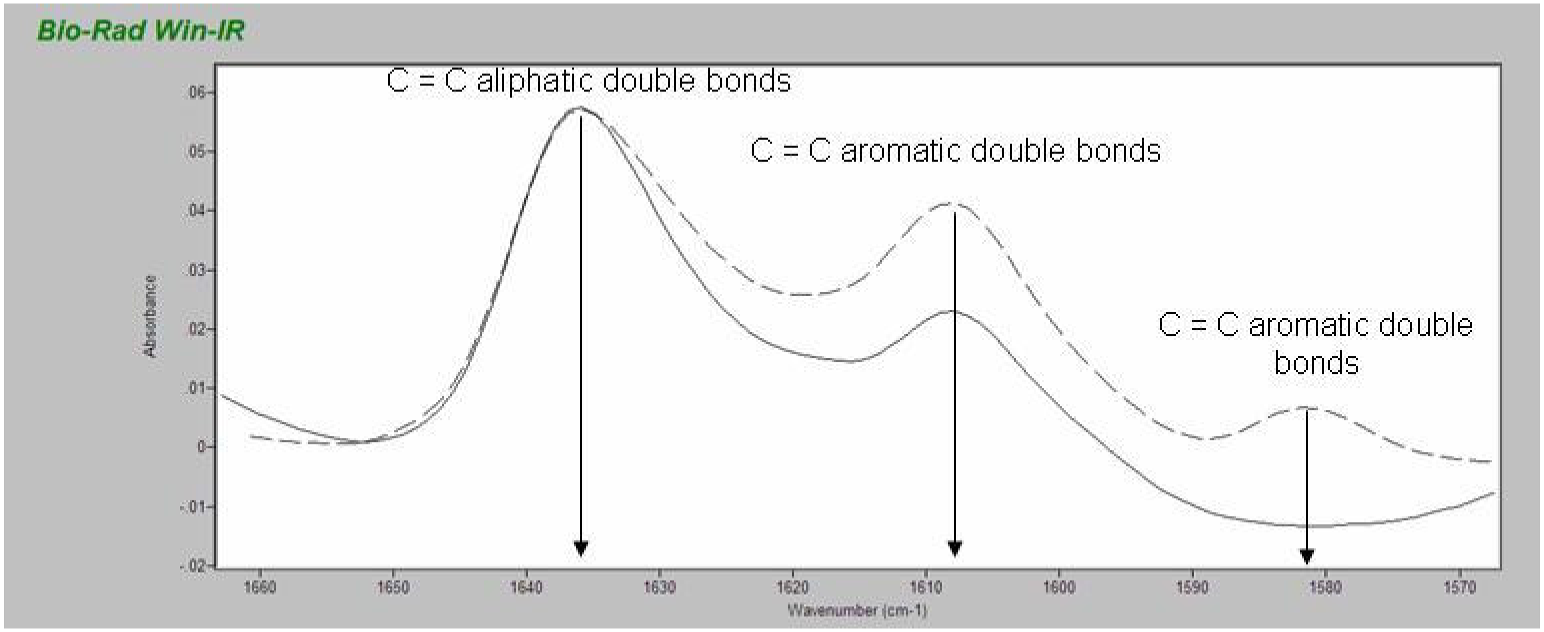
Within only a adhesive/cement system, similar letters indicate no significant difference between values (Capital letters – columns; lower case letters – rows). LC = light-cured; A2; A4 = system light-cured through 2 mm-think procured composite disc of specific shade; SC = No light exposure, total self-curing.

Table 5 Power density (mW/cm^2) measured through glass slide and through 2 mm-thick A2 / A4-shade pre-cured resin discs (Mean (SD))

Glass Slide	A2	A4
545.4 (6.3)	60.8 (0.2)	45.4 (0.3)

All values were significantly different from one another ($p < 0.05$). N = 5 replications per test condition

Fig 1



Microtensile bond strength of dual-polymerizing cementing systems to dentin using different polymerizing modes

Cesar A.G. Arrais, DDS, MS[a], Marcelo Giannini, DDS, MS, PhD[b], Frederick A. Rueggeberg, DDS, MS[c], and David H. PASHLEY, DMD, PhD[d]

Piracicaba School of Dentistry, University of Campinas, Piracicaba, Brazil; School of Dentistry, Medical College of Georgia, Augusta, Georgia, USA

[a]Graduate Student (Doctor Degree), Department of Restorative Dentistry, Piracicaba School of Dentistry, University of Campinas, Piracicaba, Brazil.

[b]Associate Professor, Department of Restorative Dentistry, Piracicaba School of Dentistry, University of Campinas, Piracicaba, Brazil.

[c]Professor and Section Director, Dental Materials, School of Dentistry, Medical College of Georgia, Augusta, Georgia, USA.

[d]Professor, Department of Oral Biology and Maxillofacial Pathology, Medical College of Georgia, Augusta, Georgia, USA.

Supported by grants CAPES BEX 0184/05-5 and FAPESP 03/03645-0.

Presented at the 35th Annual Meeting & Exhibition of the AADR, Orlando, Florida, USA, March 2006.

Reprint requests to:
Frederick Rueggeberg
Dental Materials Section, Department of Oral Rehabilitation, School of Dentistry, Medical College of Georgia, Augusta, Georgia, USA
1120, 15th Street, Room AD 3265, Georgia, USA.
Phone: (706) 721-3354Fax: (706) 721-8349
E-mail: frueggeb@mail.mcg.edu

Acknowledgments

The authors are indebted to Bisco Inc., Kerr Inc. and The Pentron Corporation for providing restorative materials, as well as to the Electron Microscopy Core Facility of the Medical College of Georgia, and to the Medical College of Georgia School of Dentistry, Augusta, GA, USA.

ABSTRACT

Statement of the problem. The effectiveness of bond strength using dual-polymerizing cementing systems (DCS, defined as the combination of dual-polymerizing bonding agents and resin cements) used with indirect restorations has not been evaluated when used solely with the auto-polymerizing mode.

Purpose. This study evaluated the in vitro microtensile bond strength (MTBS) of fourth and fifth generation DCS with indirect composite restorations either photo-polymerized or auto-polymerized.

Material and methods. Occlusal dentin surfaces of 48 human third molars were exposed and flattened. Teeth were assigned to 8 groups (n=6) according to the DCS and polymerizing modes: All Bond2/Duolink (AB2), Optibond/Nexus2 (OPT), Bond1/Lute-it (B1) and Optibond Solo Dual Cure/Nexus2 (SOLO). Bonding agents were applied to dentin surfaces and left in the unpolymerized state. Resin cements were applied to pre-polymerized resin discs (2-mm thick/Z250), which were subsequently bonded to the dentin surfaces. The restored teeth were photo-polymerized according to manufacturers' instructions (PP/XL 3000), or allowed to auto-polymerize (AP). Restored teeth were water-stored at 37°C for 24 hours and were both mesio-distally and bucco-lingually sectioned to obtain multiple bonded beams (1.2 mm^2 of cross-sectional area). Each specimen was tested in tension at a crosshead speed of 0.6mm/min until failure. Data (MPa) were analyzed by 2-way ANOVA and Tukey's post-hoc test (α=.05). Failure patterns of tested specimens were analyzed using scanning electron microscopy.

Results. MTBS means (MPa) (SD) were: AB2/PP: 36.9(6.5); AB2/AP: 32.7(7.3); B1/PP: 38.2(7.0); B1/AP: 13.0(4.2); SOLO/PP: 33.2(7.2); SOLO/AP: 23.4(3.4); OPT/PP: 30.8(7.5); OPT/AP: 13.1(5.8). AP groups showed significantly lower MTBS than PP groups (P<.0001), except for AB2, which showed no differences between polymerizing modes (P = .2608).

Conclusion. The auto-polymerizing mode of some dual polymerizing cement systems may not be effective in promoting bond strength.

Clinical implications

Dual-polymerizing bonding agents are effective in developing a strong bond to dentin when light from the light-polymerizing unit is attenuated by the overlying indirect composite resin restoration.

INTRODUCTION

Clinical success of composite and ceramic indirect restorations is attributed to the reliable bond between cementing systems (CS): defined as the combination of resin cement, bonding agent and mineralized dental tissues.[1,2] Dual-polymerizing (D) resin materials were developed to compensate for loss or absence of light due to either the distance between the activating light tip and the cementing system or to the absorption characteristics of the indirect restorative materials through which light must pass in order to photo-polymerize the adhesive resin material.[3-6]

Dual polymerizing bonding agents, being composed of a mixture of monomers and catalysts are formulated to allow polymerization without the need for polymerizing light exposure.[7-10] Therefore, light activation of the bonding agents prior to delivering an indirect restoration might not be necessary. Indirect restoration placement on the unpolymerized bonding resin layer and resin cement mixture is usually recommended in an attempt to provide adequate marginal adaptation and to avoid incomplete seating of the restoration. Moreover, the newly combined layer composed of resin cement and bonding agent components would have an overall lower content of hydrophilic monomers and higher content of hydrophobic monomers at the resin/tooth structure interface, which could provide a reduced water soluble layer when compared to only the polymerized bonding agent itself.[11-13]

Previous in vitro research demonstrated the auto-polymerizing mechanism for resin-based restorations alone is not only slower but also less effective than when using photo-activation as a supplement to the final total conversion, as noted in the higher occlusal wear, higher quantity of remaining double bonds, lower hardness, and higher solubility of dual-polymerizing resin cements.[14-22] However, little is known about the effectiveness of dual-polymerizing cementing systems (DCS – defined as the combination of a dual-polymerizing bonding agent/dual-polymerizing resin cement) in bonding indirect composite restorations when light from the light-polymerizing unit is not available or is greatly attenuated by indirect restorations.

The purpose of this study was to measure and compare the microtensile bond strength (MTBS) of fourth and fifth generation DCS when they were either allowed to auto-polymerize or when they were exposed to light through a pre-polymerized disc of composite resin. In addition, the failure site morphology was classified and compared with respect to materials and polymerizing mode type.

The research hypotheses tested were [1] fourth and fifth generation DCSs will demonstrate significantly higher MTBS when they are photo-activated than when they are allowed to auto-polymerize only, and [2] there will be no differences in MTBS among products from fourth and fifth generations within the photo- and auto-polymerizing modes.

MATERIAL AND METHODS

Indirect restorative bonding procedures

Forty-eight freshly extracted, erupted human third molars were used. The teeth were stored in saturated thymol solution at 5°C for no longer than 3 months. The research protocol was approved by the Human Assurance Committee of The Medical College of Georgia (HAC #0403333). Teeth were transversally sectioned in the middle of the crown using a diamond blade (Series 15HC Diamond, number 11-4244; Buehler Ltd, Lake Bluff, Ill) on an automated sectioning device (Isomet 2000; Buehler Ltd) under water irrigation, exposing areas of middle-depth dentin. The exposed dentin surfaces were wet-polished by machine (Supermet Grinder; Buehler Ltd) with 600-grit SiC paper (pn 810-281-PRM, Silicon Carbide PSA Discs; Leco Corp, St. Joseph, Mich) to create a flat surface with standard smear layer formation before application of the bonding agents.[23,24] Prepared teeth were divided into eight groups (n = 6).

Two fourth- and 2 fifth-generation dual-polymerizing dentin bonding agents and the corresponding dual-polymerizing resin cements from each manufacturer were used (Table I and II). Forty-eight pre-cured, photo-polymerized composite resin discs, 2 mm thick and 10 mm in diameter, (A2 shade, Z250; 3M ESPE, St. Paul, Minn) were prepared to simulate overlying laboratory-processed composite resin restorations. One surface of each pre-cured resin disc was airborne-particle abraded with 50 µm aluminum oxide particles (micron white; Danville Engineering Inc, San Ramon, Calif) for 10 seconds (air pressure: 80 psi; distance from the tip: 1.5 cm) (Comco MB 1002; COMCO Inc, Burbank, Calif). The dentin surfaces were acid etched with 35% phosphoric acid (Scotchbond Etchant; 3M ESPE) for 15 seconds, thoroughly water-rinsed, and excess water removed by absorbent paper. All bonding agents and resin cements were manipulated and applied according to manufacturers' instructions, with some exceptions as noted in Table I. The mixed resin cement pastes were applied to the airborne-particle abraded surface of the pre-polymerized composite resin disc following manufacturers' instructions, and the composite disc was positioned and fixed to the adhesive-coated dentin surface under load of 500 g for 5 minutes, where the resin cement was allowed to auto-polymerize. When the cementing materials were photo-polymerized through the pre-polymerized composite resin disc, the light activating tip was positioned against the composite resin disc and each cementing material was light-activated using a 40-second exposure from light-polymerizing unit (XL 3000; 3M ESPE). A 3-mm thick block of auto-polymerizing composite resin (shade A3/A3.5, Bisfil 2B; Bisco Inc, Schaumburg, IL) was then added to the untreated, polymerized composite resin surface to facilitate specimen gripping while the MTBS test was performed. For groups using the auto-polymerizing mode, the block of auto-polymerizing composite resin was applied to the composite resin disc only after the time stipulated for the cement's auto-polymerization reaction had passed (5 minutes).

Microtensile bond strength test

Restored teeth were stored in distilled, deionized water at 37℃ for 24 hours and were vertically, serially sectioned into several 0.8-mm thick slabs using the same cutting instrument previously described (Isomet 2000; Buehler Ltd). Each slab was further sectioned to produce bonded sticks of approximately 1.2 mm^2 in cross section. Each bonded stick was attached to the grips of a testing jig (Bisco Inc) with cyanoacrylate (Zapit; Dental Ventures of America Inc, Corona, Calif) and tested in tension on a universal testing machine (Vitrodyne V1000 Universal Tester; Chatillon, Greensboro, NC) at a crosshead speed of 0.6 mm/min until failure. After testing, the specimens were carefully removed from the fixtures with a scalpel blade and the cross-sectional area at the site of fracture was measured to the nearest 0.01 mm with a digital micrometer (Series 406; Mitutoyo America Corp., Aurora, Ill). Specimen cross-sectional area was calculated in order to present μTBS data in units of stress: MPa. A 2-way analysis of variance (ANOVA) (products and polymerizing mode) was performed. Tukey's post-hoc test was used to detect pair-wise differences among experimental groups. All statistical testing was performed at a pre-set alpha of 0.05.

Failure pattern analysis

Fractured surfaces of tested specimens were allowed to air-dry overnight at 37°C. The surfaces were then sputter-coated with gold (EMS-76M; Fullan Corp, NY) and examined in a scanning electron microscope (XL-30; Philips, Hillsboro, Ore). Failure patterns were classified as cohesive within the resin cement, adhesive along the pre-polymerized composite overlay-resin cement interface, adhesive along the dentin surface, and mixed when simultaneously exhibiting remnants of both hybrid layer and resin cement.[25]

RESULTS

Microtensile bond strength test

The statistical analysis results are displayed in Table III. The 2-way ANOVA indicated a significant effect for both main factors as well as their interaction term (*P*=.0012). The MTBS results are displayed in Table IV. No significant differences were noted when the DCSs were photo-polymerized through pre-polymerized resin discs (*P*=.1707). The systems exhibited lower MTBS when they were allowed to auto-polymerize than when they were photo-polymerized (P<.0001), except when AB2 was used. That specific product exhibited no significant difference in MTBS between auto - and photo-polymerized groups (*P*=.2608). No significant difference in MTBS was noted between AB2 and SOLO, which exhibited the highest MTBS when products were compared to each other within the auto-polymerizing mode. The systems OPT and B1 exhibited the lowest MTBS and were not significantly different.

Failure pattern analysis

Figure 1 shows the proportional prevalence (%) of the failure patterns in all experimental groups. For AB2, the predominant failure pattern was adhesive along the dentin surface for either the photo - or auto-polymerized groups (Fig. 2). The mixed failure mode exhibiting simultaneous failure within the hybrid layer and resin cement (Fig. 3) as well as adhesive failure along the dentin surface occurred at similar proportions when B1 was photo-polymerized (Fig. 1). However, the mixed failure was the predominant pattern observed when B1 was allowed to autopolymerize. Mixed failure was also the predominant failure noted when OPT was photo-polymerized. However, the predominant failure mode was adhesive along the dentin surface when OPT was allowed to auto-polymerize. When fractured surfaces of SOLO specimens were analyzed, adhesive failure along the dentin surface was the most predominant failure pattern for photo-polymerized groups, and the mixed failure mode occurred predominantly when SOLO was allowed to auto-polymerize.

DISCUSSION

This in vitro study was designed to simulate the worst clinical conditions when indirect composite resin restorations are cemented on tooth: when light from the light-polymerizing unit is compromised or completely blocked by the presence of the restorative material.[6,17,18] The results demonstrated that polymerizing mode significantly affects MTBS of DCSs, regardless of the cementing system generation: the auto-polymerizing mode promoted lower MTBS values than did the photo-polymerized mode. Therefore, the first research hypothesis that fourth and fifth generation DCSs will demonstrate significantly higher MTBS when they are photo-polymerized relative to when they are allowed to auto-polymerize, was validated for most DCSs evaluated. The only exception was observed with use of the fourth generation AB2 system, where MTBS on photo- and auto-polymerizing modes did not differ.

The fourth generation bonding agents AB2 and OPT have benzoyl peroxide and tertiary amines as the auto-polymerizing components (Table I). Presumably, these components would ensure effective monomer conversion and subsequent reliable mechanical properties of the adhesive resin within the demineralized dentin. However, only AB2 showed no significant difference in MTBS when auto-polymerized group was compared to the photo-polymerized group, while the auto-polymerized OPT group exhibited lower MTBS than photo-polymerized group. Differences in bonding agent composition as well as in monomer infiltration into the demineralized dentin could explain the differences in values observed between these 2 products. However, this speculation is invalidated since no significant differences in MTBS were observed between the fourth generation systems when photo-polymerized groups were compared to each other. Therefore, it is possible to speculate that the higher MTBS observed in this study may be related to higher monomer conversion of the DCSs. Thus, further studies are needed to evaluate and compare the monomer conversion of dual-polymerizing bonding agents with and without the incorporation of resin cements.

The fourth and fifth generation bonding agents differ considerably in composition regarding the auto-polymerizing components. Usually, fifth generation dual-polymerizing bonding agents do not only have benzoyl peroxide/tertiary amines as auto-polymerizing components, but contain co-initiators such as benzene sulfinic acid sodium salt (Table I). Two fith generation bonding agents were evaluated in this study: B1, which has benzoyl peroxide/tertiary amines, and SOLO, which contains a benzene sulfinic acid sodium salt. It has been reported that benzene sulfinic acid sodium salt is added to fifth generation dual-polymerizing bonding agents to avoid chemical incompatibility between such bonding agents and dual-polymerizing resin cements.[7-9] Therefore, the lack of sulfinic sodium salts in B1 may have allowed the reaction between tertiary amines and acidic monomers to form a charge transfer complex (CT complex),[9] which compromises their ability as reducing agents in redox reaction[7,8,10] and lowers bond strength. As a consequence, a poor polymerization reaction is expected from the combined adhesive/resin cement layer. This hypothesis seems confirmed by the fact that the mixed failure mode was the predominant failure pattern of B1 specimens (Fig. 1), and may also explain why the auto-polymerized B1 group showed one of the lowest MTBS values in this study. These differences in MTBS among auto-polymerized groups and the lack of significant differences among photo-polymerized DCSs systems, regardless of the generation, validated the second research hypothesis, which anticipated that there would be no significant differences in MTBS between DCS generations.

The higher MTBS of SOLO when compared to that of the other fifth generation DCS may confirm the partial effectiveness of benzene sulfinic sodium salts in reducing the chemical incompatibility between fifth generation bonding agents and their dual-polymerizing resin cements as previously reported.[7,10] However, auto-polymerized SOLO demonstrated lower MTBS than the photo-polymerized mode. Hoffman et al[19] demonstrated that the auto-polymerizing mode compromised mechanical properties such as flexural strength, modulus of elasticity, and surface hardness of the dual-polymerizing resin cement Nexus 2, which may have consequently affected the MTBS of SOLO when the resin cement was allowed to auto-polymerize. The predominant failure pattern in this experimental group was adhesive along the adhesive dentin surface, although a considerable proportion of mixed failure mode was also observed in this group (Fig. 1). Therefore, it is difficult to determine if the lower MTBS in the auto-polymerized SOLO group was due to the partial effectiveness of sulfinic sodium salts or to the compromised mechanical properties of the resin cement. Monomer conversion analysis of fifth generation DCSs, either with or without the presence of co-initiator in their compositions, could shed some evidence about the limitations of these products.

Other factors may also be involved in the effectiveness of monomer conversion and development of mechanical properties of dual-polymerizing bonding agents when light from the light-polymerizing unit is not available. Tanoue et al[22] observed higher solubility and water absorption in some dual-polymerizing resin cements when they were allowed to auto-polymerize. All bonding agents evaluated in this study were applied using the wet bonding technique. A slower polymerization reaction is expected when DCSs are allowed to auto-polymerize,[20,21] and the increased solubility of the adhesive resin within the hybrid layer may have decreased monomer conversion, and consequently the short- or long-term bond strength of the adhesive interface.[11] Solubility is also related to the composition of adhesive resin within the hybrid layer, as higher concentrations of hydrophobic monomer may contribute to lower solubility values and higher bond strength.[12,13] It is possible that the composition of the hybrid layer may vary according to the ability of some resin cementing system components to penetrate into this layer and change the ratio between the concentration of hydrophilic and hydrophobic monomers. Therefore, water absorption by the adhesive resin within the hybrid layer may depend on the ability of the resin cement system components to penetrate into the hybrid layer and to mix with the bonding agent prior to polymerization. Such a mixture within the demineralized dentin prior to polymerization may substantially reduce solubility. However, as there are no data about the penetration of such components into the dentin, further studies are necessary to evaluate the morphology, chemical composition of the hybrid layer, as well as long-term bond strength of indirect composite resins bonded to dentin with different DCS products.

This in vitro study evaluated the MTBS of dual-polymerizing resin cements and adhesive systems in laboratory conditions. Therefore, factors such as dentinal fluid movement and internal stress related to the cavity configuration for indirect restorations were not simulated in this methodology. Therefore, further studies are necessary to evaluate the influence of those factors on the mechanical properties of the adhesive interface created by such cementing systems bonded to teeth.

Based on the findings of this current study, it is evident that care must be taken when selecting a dual-polymerizing cementing system for indirect restorative procedures, since some cementing systems require light activation of the bonding agent itself to ensure proper bond strength to dentin. Conversely, other systems can confidently rely on solely the auto-polymerizing mode. These products are indicated in clinical conditions where limited light will reach the interface to be polymerized: both intracoronally as well as within a root canal.

CONCLUSION

Based on the limitations imposed in this study, the following conclusions were drawn:

1. Some fourth and fifth generation dual-polymerizing resin cementing systems, Optibond, Optibond Solo Dual Cure, and Bond 1, demonstrate significantly higher bond strengths when they are photo-polymerized than when they were allowed to auto-polymerize.
2. There were no differences in MTBS between fourth and fifth generation cementation systems within photo-polymerized modes, but significant differences were noted in the auto-polymerizing modes. Differences in auto-polymerized

groups were product dependent: All Bond 2 and Optibond Solo presented the highest MTBS, and Optibond and Bond 1 exhibited the lowest values.

REFERENCES

1. Inokoshi S, Willems G, Van Meerbeek B, Lambrechts P, Braem M, Vanherle G. Dual-cure luting composites: Part I: Filler particle distribution. J Oral Rehabil 1993;20:133-46.

2. Sjogren G, Molin M, van Dijken J, Bergman M. Ceramic inlays (Cerec) cemented with either a dual-cured or a chemically cured composite resin luting agent. A 2-year clinical study. Acta Odontol Scand 1995;53:325-30.

3. Milleding P, Ortengren U, Karlsson S. Ceramic inlay systems: some clinical aspects. J Oral Rehabil 1995;22:571-80.

4. Nathanson D. Etched porcelain restorations for improved esthetics, part II: Onlays. Compendium 1987;8:105-10.

5. Strang R, McCrosson J, Muirhead GM, Richardson SA. The setting of visible-light-cured resins beneath etched porcelain veneers. Br Dent J 1987;163:149-51.

6. Rasetto FH, Driscoll CF, Prestipino V, Masri R, von Fraunhofer JA. Light transmission through all-ceramic dental materials: a pilot study. J Prosthet Dent 2004;91:441-6.

7. Sanares AM, Itthagarun A, King NM, Tay FR, Pashley DH. Adverse surface interactions between one-bottle light-cured adhesives and chemical-cured composites. Dent Mater 2001;17:542-56.

8. Ruyter IE. Unpolymerized surface layers on sealants. Acta Odontol Scand 1981;39:27-32.

9. Bowen RL, Cobb EN, Rapson JE. Adhesive bonding of various materials to hard tooth tissues: improvement in bond strength to dentin. J Dent Res 1982;61:1070-6.

10. Yamauchi J. Study of dental adhesive containning phosphoric acid methacrylate monomer. Japanese Journal of Dental Materials 1986;5:144-54.

11. De Munck J, Van Meerbeek B, Yoshida Y, Inoue S, Vargas M, Suzuki K, et al. Four-year water degradation of total-etch adhesives bonded to dentin. J Dent Res 2003;82:136-40.

12. Yiu CK, Garcia-Godoy F, Tay FR, Pashley DH, Imazato S, King NM, et al. A nanoleakage perspective on bonding to oxidized dentin. J Dent Res 2002;81:628-32.

13. Jacobsen T, Soderholm KJ. Some effects of water on dentin bonding. Dent Mater 1995;11:132-6.

14. Blackman R, Barghi N, Duke E. Influence of ceramic thickness on the polymerization of light-cured resin cement. J Prosthet Dent 1990;63:295-300.

15. Hasegawa EA, Boyer DB, Chan DC. Hardening of dual-cured cements under composite resin inlays. J Prosthet Dent 1991;66:187-92.

16. Peutzfeldt A. Dual-cure resin cements: in vitro wear and effect of quantity of remaining double bonds, filler volume, and light curing. Acta Odontol Scand 1995;53:29-34.

17. Braga RR, Cesar PF, Gonzaga CC. Mechanical properties of resin cements with different activation modes. J Oral Rehabil 2002;29:257-62.

18. Rueggeberg FA, Caughman WF. The influence of light exposure on polymerization of dual-cure resin cements. Oper Dent 1993;18:48-55.

19. Hofmann N, Papsthart G, Hugo B, Klaiber B. Comparison of photo-activation versus chemical or dual-curing of resin-based luting cements regarding flexural strength, modulus and surface hardness. J Oral Rehabil 2001;28:1022-8.

20. Asmussen E. Setting time of composite restorative resins vs. content of amine, peroxide, and inhibitor. Acta Odontol Scand 1981;39:291-4.

21. Lee IB, Um CM. Thermal analysis on the cure speed of dual cured resin cements under porcelain inlays. J Oral Rehabil 2001;28:186-97.

22. Tanoue N, Koishi Y, Atsuta M, Matsumura H. Properties of dual-curable luting composites polymerized with single and dual curing modes. J Oral Rehabil 2003;30:1015-21.

23. Tay FR, Pashley DH. Aggressiveness of contemporary self-etching systems. I: Depth of penetration beyond dentin smear layers. Dent Mater 2001;17:296-308.

24. Montes MA, de Goes MF, Sinhoreti MA. The in vitro morphological effects of some current pre-treatments on dentin surface: a SEM evaluation. Oper Dent 2005;30:201-12.
25. Mak YF, Lai SC, Cheung GS, Chan AW, Tay FR, Pashley DH. Micro-tensile bond testing of resin cements to dentin and an indirect resin composite. Dent Mater 2002;18:609-21.

Table I. Manufacturers and compositions of all 4th and 5th generation cementing systems

Product (code) (Manufacturer)	Composition (manufacturer provided) (Batch Number)	Manufacturer's Instructions and exceptions
All Bond 2 (AB2) (Bisco Inc.)	*Primer A:* acetone; ethanol; Na-N-tolylglycine; glycidylmethacrylate (0500003574); *Primer B:* acetone; ethanol; biphenyl dimethacrylate (0500003579); *Pre-Bond Resin:* Bis-GMA, TEGDMA; benzoyl peroxide; BHT (0500004345).	Mix primers A and B. Apply 5 consecutive coats to dentin; Dry all surfaces for 5-6 seconds with an air syringe; Light activate 20 seconds*; Apply thin layer of Pre-Bond Resin immediately prior to cementation. Air thin. Do not light activate.
Bond 1 (B1) (Pentron Corp.)	*Activator:* Methacrylate monomers in Ethanol and/or Acetone, Benzoyl Peroxide Unknown, Acetone (128878). *Resin:* Mixture of PMGDM, a condensation product of PMDA and Glycerol, Dimethacrylate HEMA and TMPTMA in ethanol and/or acetone with photo initiator, amine accelerator & stabilizer, Pyromellitic Dianhydride (129121).	Mix one drop of *Bond1* Dual Cure Activator with 2 drops of *Bond1* Primer/Adhesive. Using a fully saturated brush tip each time, apply two coats of *Bond1* Primer/Adhesive to tooth within 10 seconds; Apply a gentle stream of air for a minimum of ten (10) seconds. Hold air syringe 1 inch from site, positioned so as not to disturb resin surface. (Avoid excess of *Bond1* Primer/Adhesive in internal line angles or point angles).
Optibond (OPT) (Kerr Corp.)	*Primer*: Ethyl Alcohol, Alkyl Dimethacrylate Resins, Water (423435). *Dual Cure Paste (3B)*: Uncured Methacrylate Ester Monomers; Triethylene Glycol Dimethacrylate (424560); Inert glass filler, pigment and stabilizers. *Dual Cure Activator Resin (3A):* Uncured Methacrylate; Ester Monomers; Benzoyl Peroxide (423073).	Apply Optibond Prime (bottle 1) to dentin and enamel surfaces with microbrush, scrubbing the surface for thirty (30) seconds; Air dry for 5 seconds; Dispense Optibond Dual Cure paste (3B) and 1 drop of Dual Cure Activator (3A) and thoughtfully mix them for 15 seconds; Apply a thin coat of the mixed dual cure to the dentin surface.; Do not air thin and do not light activate it.
Optibond Solo (SOLO) (Kerr Corp.)	*Adhesive Resin:* ethyl alcohol; Bis-GMA; HEMA; GPDM; photoinitiators; barium aluminoborosilicate glass; fumed silica (silicon dioxide); sodium hexafluorosilicate. *Activator:* ethyl alcohol; alkyl dimethacrylate resins; benzene sulfinic acid sodium salt.	Dispense one drop of Optibond Solo Plus and Optibond Solo Activator into a disposable mixing well. Mix for 3s; Apply mixture to dentin with a light brushing for 15s to cover dentin surface; Lightly air thin for 3s; Light activated for 20s*.

TEGDMA: triethylene glycol dimethacrylate; Bis-GMA: bisphenol A diglycidyl ether methacrylate; PMDA: pyromellitic dianhydride; PMGDM: pyromellitic glycerol dimethacrylate; BHP: butylated hydroxytoluene; TMPTMA: trimethylolpropane trimethacrylate; HEMA: 2-hydroxyethyl methacrylate; GPDM: glycerophosphoric acid dimethacrylate.

* The bonding agents were not photo-polymerized before the cementation of indirect composite resin disc.

Table II. Brand, composition and batch number of the dual-polymerizing resin cements used

Product (Manufacturer)	Composition	Batch Number
Duolink (Bisco Inc., Schaumberg, IL)	*Base:* Bis-GMA; TEGDMA; glass filler; urethane dimethacrylate. *Catalyst:* Bis-GMA; TEGDMA; glass filler.	0500003751
Nexus 2 (Kerr Corp., Orange, CA)	Monomers of methacrylic acid esters, Ba–Al –borosilicate glass, chemical and photoinitiators.	Base:423638 Cataly.:423975
Lute-It! (Pentron Corp., Wallingford, CT)	In both Base & Catalyst: UDMA, HDDMA, Amine and inorganic pigments (in base only), Benzoyl Peroxide (in Catalyst only), UV Stabilizers (in both base and catalyst), Barium Glass, Inorganic Fluoride, Borosilicate Glass, Silane Silica Zirconia.	Base:130666 Cataly.:126388

TEGDMA: Triethylene glycol dimethacrylate, Bis-GMA: Bisphenol A diglycidyl ether methacrylate, UDMA: Urethane dimethacrylate, HDDMA: 1,6-hexanediol dimethacrylate.

Table III. The 2-way analysis of variance

Source	DF	Type III SS	Mean Square	F Value	P value
Products	3	1064.93	354.98	8.94	0.0001
Polymerizing mode	1	2419.68	2419.68	2419.68	<.0001
Products * Polymerizing mode	3	758.30	252.76	6.37	0.0012

DF: Degree of Freedom.

Table IV. Microtensile bond strength (MPa) of dual-polymerizing cementing systems either photo-polymerized or allowed to auto-polymerize (mean (sd))

Bonding agent/cement (generation) (code)	Photo-polymerized	Auto-polymerized
All Bond 2 / Duolink (4th generation) (AB2)	36.9 (6.5)Aa	32.7 (7.3)Aa
Optibond Solo Dual Cure / Nexus 2 (5th generation) (SOLO)	33.2 (7.2)Aa	23.4 (3.4)Ab
Bond 1 / Lute-it (5th generation) (B1)	38.2 (7.0)Aa	13.0 (4.2)Bb
Optibond / Nexus 2 (4th generation) (OPT)	30.8 (7.5)Aa	13.1 (5.8)Bb

Values of groups having similar letters were not significantly different (Capital letters = column; lower case letter = rows). N = 6 specimens per experimental group.

LEGENDS

Fig. 1. Proportional prevalence (%) of failure patterns for all experimental groups.

Fig. 2. (a) Fractured end of a specimen restored with AB2 exhibiting failure pattern classified as adhesive along the dentin surface (original magnification X142). (b) Fractures located predominantly within the hybrid layer (HL) are seen (original magnification X1000). This failure pattern was observed predominantly in the AB2 group, in auto-polymerized OPT, and in photo-polymerized SOLO.

Fig. 3. (a) A mixed failure mode is seen exhibiting the coincident presence of hybrid layer (HL) and resin cement (RC). This failure mode was most prominent in auto-polymerized B1 and SOLO, as well as in photo-polymerized OPT (original magnification X135). (b) Higher magnification demonstrating HL and RC from the same fractured surface observed in Figure 3A (original magnification X710).

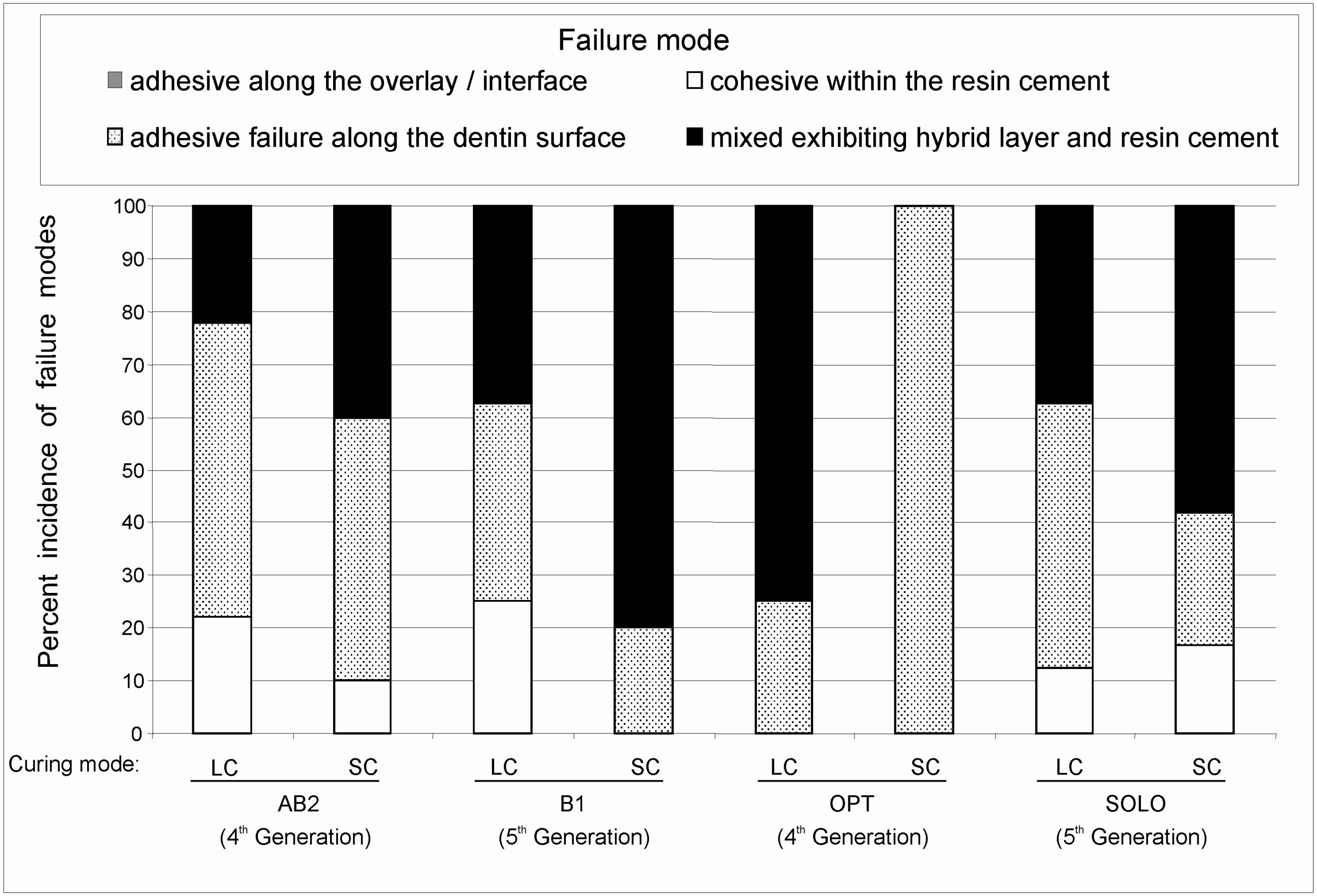

Failure mode
▪ adhesive along the overlay / interface
☐ cohesive within the resin cement
▨ adhesive failure along the dentin surface
■ mixed exhibiting hybrid layer and resin cement
Percent incidence of failure modes
100
90
80
70
60
50
40
30
20
10
0
Curing mode:
LC
SC
LC
SC
LC
SC
LC
SC
AB2
(4th Generation)
B1
(5th Generation)
OPT
(4th Generation)
SOLO
(5th Generation)

Figure 1

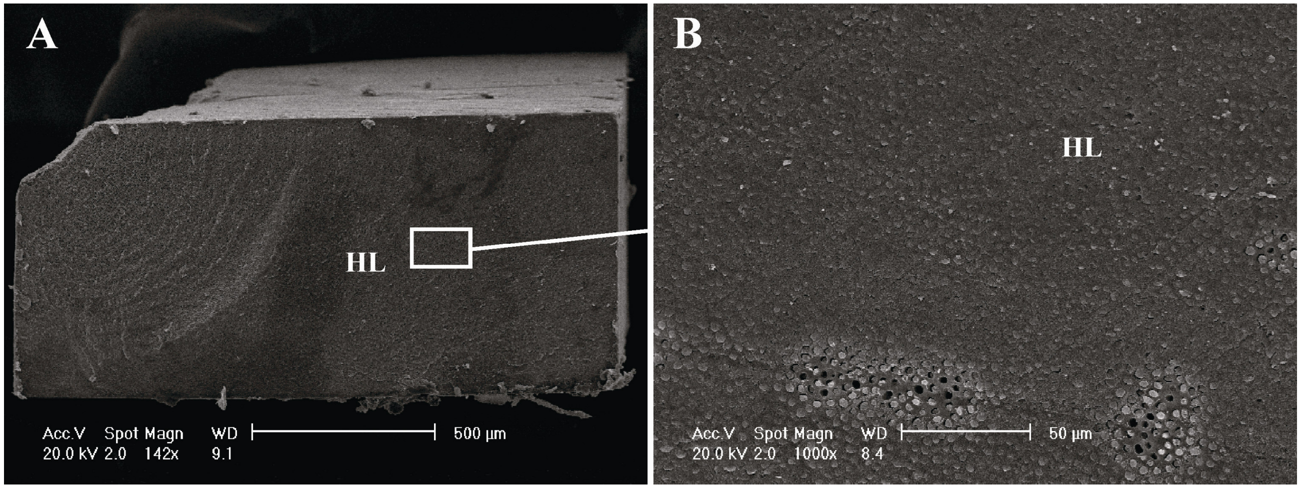


Figure 2

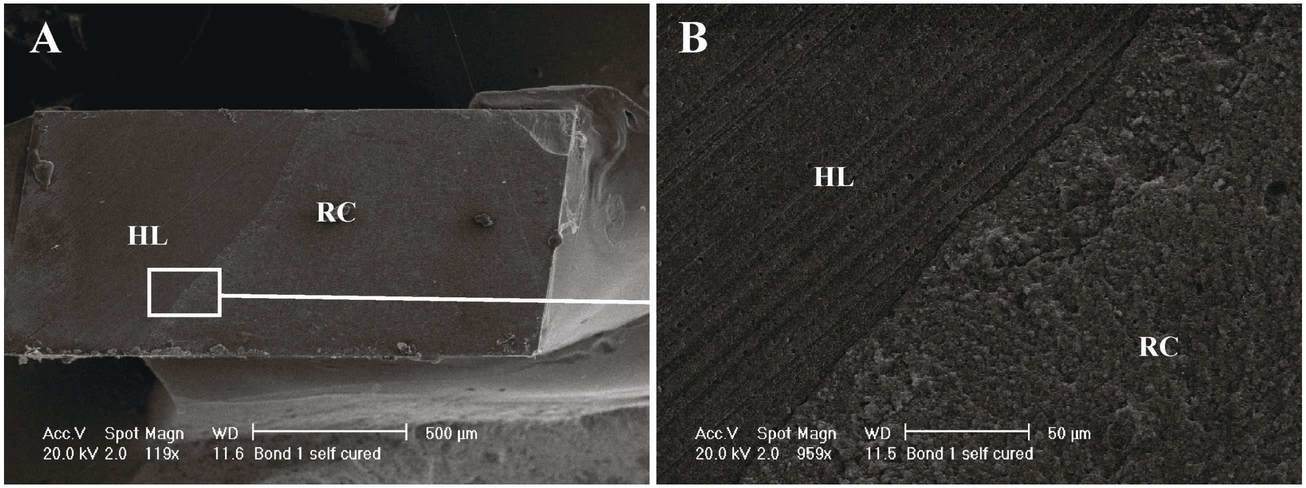


Figure 3

DEGREE OF CONVERSION OF ADHESIVE SYSTEMS LIGHT-CURED BY LED AND HALOGEN LIGHT

Cesar Augusto Galvão ARRAIS[1] / Fenelon Martinho PONTES[2] / Luis Presley Serejo dos SANTOS[2] / Edson Roberto LEITE[2] / Marcelo GIANNINI[1]

[1]Department of Restorative Dentistry, Piracicaba School of Dentistry, State University of Campinas, Piracicaba - SP, Brazil.

[2]LIEC-Department of Chemistry, UFSCar-Federal University of São Carlos, São Carlos, SP, Brazil.

Short Tittle: LED effects on adhesive resin conversion

Corresponding author: Marcelo Giannini
Department of Restorative Dentistry / Operative Dentistry Section
Piracicaba School of Dentistry, UNICAMP
Av. Limeira, 901 – Areião - Piracicaba / SP
CEP 13414-900 Brazil

Telephone: 55 19 34125338

Fax: 55 19 34125218

E-mail: giannini@fop.unicamp.br

ABSTRACT

This study evaluated the effect of blue light emitting diode (LED) and conventional halogen light (HAL) on the degree of conversion (DC) of an etch-and-rinse Single Bond adhesive system (SB) and a mixture composed of primer solution and resin bond from self-etching Clearfil SE Bond adhesive system (CB) using Fourier Transform Infrared Analysis (FTIR). Adhesives were applied to KBr pellet surfaces and FTIR analyses were performed before and after photo-activation for 10 seconds with either LED (Freelight 1 – 400mw/cm^2) or HAL (XL 3000 – 630mw/cm^2) light-curing units (n=8). Additional FTIR spectra were obtained from photo-activated samples stored in distilled water for 1 week. The DC was calculated by comparing the spectra obtained from adhesive resins before and after photo-activation. The results were analyzed by two-way split-plot ANOVA and Tukey's test ($p<0.05$). Both adhesive systems exhibited low DC (%) immediately after photo-activation (SB/HAL: 18.7±3.9; SB/LED: 13.5±3.3; CF/HAL: 13.6±1.9; CF/LED: 6.1±1.0). The DC of samples light-cured with LED was lower than DC of those light-cured with HAL, immediately after light curing and after 1 week (SB/HAL: 51.3±6.6; SB/LED: 50.3±4.8; CF/HAL: 56.5±2.9; CF/LED: 49.2±4.9). The LED curing unit used to photo-activate the adhesive resins promoted lower DC than when HAL curing unit was used.

Keywords: LED, halogen lamp, degree of conversion, adhesive system.

INTRODUCTION

For many years quartz-tungsten-halogen bulbs have been used as the lighting source to photo-activate visible-light cured composite resins. However, some factors may compromise the performance of halogen light curing units (LCUs), such as fluctuations in the line voltage, the condition of the bulb and filter, contamination of the light guide, damage to the fiber-optic bundle as well as bulb overheating within the unit. These factors can contribute to reduce the efficiency and lifetime of halogen lamps, leading to poorly polymerized composite resins with impaired mechanical properties (1).

Blue light emitting diode (LED) technology has been indicated as an alternative to conventional halogen lights. LEDs LCUs consume little power in operating and do not require filters to produce blue light. Moreover, the use of semiconductors for light emission instead of hot metal filaments found in halogen bulbs generate less heat and undergo little degradation over time. The gallium nitride LEDs produce a narrow wavelength peak around 470 nm, which matches the absorption peak value of camphorquinone, the most common photoabsorbing compound that initiates the polymerization of resin monomers in dental restorative composites (2).

Some mechanical and physical properties of resin composites light-cured by LED have been reported in the dental literature, such as compressive and flexural strength, hardness, degree of conversion and depth of cure. Although LED polymerization technology tends to reach the performance level of halogen LCUs (3-6), additional studies are needed to determine the degree of conversion of dental resin-based materials (7,8).

Optimal monomer infiltration into the demineralized collagen network and achievement of high degrees of monomer conversion are crucial factors for establishing long-lasting resin/dentin bonding (9). Some factors might affect the conversion of resin monomer, such as the residual water or organic solvents, and the quality of the light source applied to photo-activate the adhesive systems. Although there are many reports about the effects of LED on composite resins, little-to-no studies exist about the efficiency of LED on the degree of conversion of adhesive systems (10). This study evaluated the degree of monomer conversion of two adhesive systems photo-activated with LED and halogen LCUs, using Fourier Transform Infrared (FTIR) analysis. The null hypothesis was that there is no difference in the degree of conversion when adhesive systems are photo-activated by LED or halogen LCUs.

MATERIALS AND METHODS

The adhesive systems investigated were: Single Bond (3M ESPE, St. Paul, MN, USA) and Clearfil SE Bond (Kuraray Medical Inc., Kurashiki, Okayama, Japan). Their compositions are described in Table 1. Two commercially available LCUs (Table 2) were tested: XL 3000 halogen-based (3M ESPE – light intensity: 550-630 mw/cm^2) and Elipar Freelight 1 LED-based (3M ESPE - light intensity: 400 mw/cm^2). Thus, four experimental groups (n = 5) were formed and studied, according to the factors under study (adhesive system and curing unit).

For FTIR analysis of Single Bond, one drop of the adhesive resin solution was placed into mixing well. An applicator tip was dipped into adhesive solution and the adhesive was applied to the surface of a potassium bromide pellet. Single Bond adhesive was air dried for 10 seconds, following the manufacture's instructions, before curing for 10 seconds. Clearfil SE Bond specimens were prepared by mixing four drops of bonding resin and one drop of primer in a mixing well and air dried for 90 seconds. One adhesive layer was applied using an applicator tip and light-cured for 10 seconds. The adhesive systems were light cured without Mylar strip over adhesive layer.

FTIR spectra of non-polymerized adhesive solution were obtained using 20 scans at 4 cm^{-1} in the transmittance mode (Equinox 55, Bruker Optik GmbH, Ettlingen, Germany). Additional FTIR spectra were obtained immediately after 10 second light-curing and after sample storage in distilled water for 1 week.

For calculating the DC, the aliphatic carbon-to-carbon double bond absorbance peak intensity located at 1638 cm^{-1} and that for the aromatic component located at 1608 cm^{-1} (aromatic) were compared in each spectrum before and after the polymerization reaction, and monomer conversion was determined using the following equation (11):

$$(\% \, C = C) = \frac{[\text{abs (aliphatic C = C)/abs (aromatic C} \ldots \text{C)] polymer}}{[\text{abs (aliphatic C = C)/abs (aromatic C} \ldots \text{C)] monomer}} \times 100$$

(% C = C): Percentage of remaining carbon double bonds.

abs : absorbance

The DC was obtained by subtracting the percentage of remaining carbon double bonds (% C = C) from 100%. Conversion data was analyzed using two-way split-plot ANOVA and Tukey's post-hoc test ($\alpha = 0.05$).

RESULTS

Tables 3, 4 and 5 show the degree of conversion means and standard deviations for adhesive systems light cured with halogen and LED-based LCUs. Two-way ANOVA revealed that there were statistically significant differences for the factor "adhesive system" ($p = 0.00001$), for the factor "curing unit" ($p = 0.00001$) and for factor interactions ($p = 0.01432$).

Tukey test showed that the degree of conversion of Single Bond was higher than Clearfil SE Bond photo-activated with LED-based LCUs. The monomer conversion of both Single Bond and Clearfil SE Bond adhesive systems was affected by LCU type (Table 3). The adhesive systems exhibited low degree of conversion immediately after photo-activation with both LCUs (Tables 4 and 5). The degree of conversion of samples light-cured with LED was lower than those light-cured with halogen light, either immediately after light curing or after 1 week stored (Tables 3, 4 and 5).

Figure 1 shows the spectrum sites obtained from Single Bond and Clearfil SE Bond before and immediately after light curing, as well as after 1 week of storage in water. These sites were used to calculate the degree of conversion. Figures 1A and 1B exhibit the spectrum sites obtained from Single Bond light cured by halogen light and LED LCUs, respectively, while Figures 1C and 1D corresponds to the sites from Clearfil SE Bond light cured by halogen light and LED LCUs. There was little reduction in the peak located at 1638 cm^{-1} after 10 seconds of light curing for both adhesive systems. Compared to the spectra obtained from samples immediately after-curing by halogen light, the spectra obtained from samples light cured with LED demonstrate an apparently smaller reduction in the peak corresponding to carbon-double bonds (1638 cm^{-1} - Figures

1B and 1D). After 1 week of storage in water, a pronounced reduction in the same peak was observed for both Single Bond and Clearfil SE Bond.

DISCUSSION

The degree of monomer conversion depends on the output and wavelength of the light, exposure time and composition of light-activated resin-based material. In this current study, the resin-based materials tested were adhesive systems, which were light cured with two commercially available LCUs. The results indicated that the LED-based LCU did not polymerize the adhesive systems at different times of post-light curing like conventional halogen lamp does, therefore, the null hypothesis was rejected.

One possible reason for this result may be the difference in light intensities. The light intensity of the halogen LCU evaluated in this study is approximately 600 mW/cm^2, while the LED LCU has light intensity of approximately 400 mW/cm^2. The higher light intensity increases the peak height at 470 nm and more camphorquinone molecules will be excited. As a consequence, more free radicals are generated and faster monomer conversion will occur, resulting in higher degree of conversion in shorter time (12). Some studies have suggested that halogen light still produce greater curing energy and higher degree of composite monomer conversion than the first generation of LED lights (7,8,13).

Halogen LCUs generate heat during operation, increasing the temperature on the surface. Based on the fact that the adhesive systems are spread into a layer thinner than that of restorative composites prior to light curing (10), the rise of surface temperature occurred during polymerization can additionally improve the rate of polymerization. The heat can be absorbed, increasing the molecular movements and the collisions, which can contribute to increase the degree of conversion (1,6,14,15).

A great amount of unpolymerized monomers from Clearfil SE Bond adhesive were detected by FTIR analysis immediately after LED photo-activation.

Regardless of the lower power density emitted by LED (7,8,13), differences in resin adhesive composition and sample preparation might have affected the degree of conversion when LED LCU was tested. The mixture of Bond and Primer of Clearfil SE Bond results in a solution with low pH (approximately 2) and high water content, which can impair the polymerization reaction of the adhesive. The Clearfil SE Bond samples were composed of the mixture of four drops of Bond and one drop of Primer in an attempt to reduce the water content and increase the monomer pH that allows the polymer conversion to occur. When applied to tooth surface, the self-etching primer acidity can be buffered by mineral content of dentin and enamel (18), allowing the higher monomer conversion. The changes for preparations of Clearfil SE Bond samples, such as reduction in the water content from Primer solution and the increase in Bis-GMA content, might have altered the adhesive material, which would modify the maximal rate of conversion and the result of the polymerization reaction (19).

Like when adhesive systems are applied clinically, the contact between resin adhesive and atmospheric oxygen was not avoided during the photo-activation of adhesive samples (16,17). This might explain the low degree of conversion observed in the thin cured adhesive layers immediately after light exposition by both LCUs tested. Thus, an uncured adhesive layer affected by oxygen inhibition may form poor polymer chain in the hybrid layer, reducing the longevity of tooth-composite bonding (9).

On the other hand, FTIR analysis of adhesive samples after 1 week exhibited a pronounced increase in degree of conversion compared to the initial values for both LCUs used and adhesive systems evaluated. A possible explanation was that the polymerization reaction might last for periods longer than 24 hours (12). Moreover, based on the fact that incomplete conversion of monomers could result in increased adhesive resin solubility, the water immersion could lead to the removal of the oxygen-inhibited resin layer from the surface of lighted-cured samples stored for one week (20). Therefore, FTIR analysis of samples without uncured layer will only count the amount of residual carbon double bonds from the cured layer and those from the uncured layer that can be also covalently bound to the polymer chain with further potential to react chemically and cannot leach out (1).

Within the limits of the methodology employed in this study, we concluded that the measurements of the degree of monomer conversion showed that LED LCU did not produce similar performance level of conventional halogen LCU for adhesive systems tested. Considering the low initial degree of adhesive monomer conversion into polymer and LED LCU performance, concerns related to the formation of high quality hybridization zones arise when the adhesive systems are applied to deep or unfavorable cavity preparations where curing energy decreases significantly. This condition can have clinical significance on the durability of the adhesive.

ACKNOWLEDGEMENTS

This study was supported by FAPESP # 03/03645-0.

GRAU DE CONVERSÃO DE SISTEMAS ADESIVOS FOTOATIVADOS POR LED E LUZ HALÓGENA

RESUMO

Este estudo avaliou a influência de sistemas de fotoativação no grau de conversão (GC) de adesivos odontológicos através da análise Infravermelha Transformada de Fourier (FTIR). Os sistemas adesivos Single Bond (SB) e Clearfil SE Bond (CF) foram aplicados em pastilhas de brometo de potássio e fotoativados com luz halógena (XL 3000 – 630 mw/cm^2)(HA) e LED (Elipar Freelight 1 – 400 mw/cm^2) por 10 segundos. Foram obtidos espectros de FTIR antes e imediatamente após a fotoativação, e tambem após 1 semana de armazenamento em água destilada (37ºC) (n=8). Calculou-se o GC comparando-se a razão entre os picos das bandas 1609 e 1638 (C=C) dos espectros, antes e após a fotoativação. Os resultados de GC foram submetidos à ANOVA e ao teste de Tukey (5%). O GC (%) obtido imediatamente após a fotoativação com LED foi inferior ao obtido utilizando-se HAL (SB/HAL: 18.7±3.9; SB/LED: 13.5±3.3; CF/HAL: 13.6±1.9; CF/LED: 6.1±1.0). Após uma semana foi observado um aumento significativo no GC de todos os grupos, porém os valores dos grupos fotoativados com LED mantiveram-se inferiores aos obtidos com HAL (SB/HAL: 51.3±6.6; SB/LED: 50.3±4.8; CF/HAL: 56.5±2.9; CF/LED: 49.2±4.9). O GC dos adesivos fotoativados com LED foi inferior ao observado após fotoativação com HA, imediatamente após fotoativação como após 1 semana de armazenamento em água.

Keywords: LED, luz halógena, grau de conversão, sistemas adesivos.

REFERENCES

1. Rueggeberg FA. Contemporary issues in photocuring. Compend Contin Educ Dent 1999;20:S4-15. Supplement 25.
2. Burgess JO, Walker RS, Porche CJ, Rappold AJ. Light curing – an update. Compend Contin Educ Dent 2002;23:889-906.
3. Stahl F, Ashworth SH, Jandt KD, Mills RW. Light-emitting diode (LED) polymerization of dental composites: flexural properties and polymerization potential. Biomaterials 2000;21:1379-1385.
4. Jandt KD, Mills RW, Blackwell GB, Ashworth SH. Depth of cure and compressive strength of dental composites cured with blue light emitting diodes. Dent Mater 2000;16:41-47.
5. Nomura Y, Teshima W, Tanaka N, Yoshida Y, Nahara Y, Okazaki M. Thermal analysis of dental resins cured with blue light-emitting diodes. J Biomed Mater Res 2002;63:209-213.
6. Hofman N, Hugo B, Klaiber B. Effect of irradiation type (LED or QTH) on photo-activacted composite shrinkage strain kinetics, temperature raise and hardness. Eur J Oral Sci 2002;110:471-479.
7. Knezevic A, Tarle Z, Meniga A, Sutalo J, Pichler G, Ristic M. Degree of conversion and temperature rise during polymerization of composite resin samples with blue diodes. J Oral Rehabil 2001;28:586-591.
8. Dunn WJ, Bush AC. A comparison of polymerization by light-emitting diode and halogen-based light-curing units J Am Dent Assoc 2002;133:335-341.
9. Reis AF, Arrais CAG, Novaes PD, Carvalho RM, De Goes MF, Giannini M. Ultramorphological analysis of resin-dentin interfaces produced with water-based single-step and two-step adhesives: nanoleakage expression. J Biomed Mater Res 2004;71B:90-98.
10. De Goes MF; Giannini M; Rueggeberg FA. Conversion of dentin bonding agents mixed with composite. J Dent Res 2004;83:SI, Abstract 556.

11. Ferracane JL, Greener EH. Fourier transform infrared analysis of degree of polymerization in unfilled resins--methods comparison. J Dent Res 1984;63:1093-1095.
12. Halvorson RH, Erickson RL, Davidson CL. Energy dependent polymerization of resin-based composite. Dent Mater. 2002;18:463-469.
13. Nomoto R. Effect of light wavelength on polymerization of light-cured resins. Dent Mater J 1997;16:60-73.
14. Kloosterboer JG, Van de Hei GMM, Gossink RG, Dortant GCM. The effects of volume relaxation and thermal mobilization of trapped radicals on the final conversion of photopolymerized diacrylates. Polymer Comm 1984;25:322–325.
15. Wendt Jr SL. The effect of heat used as a secondary cure upon the physical properties of three composites resins. I. Diametral tensile strength, compressive strength and marginal dimensional stability. Quintessence Inter 1987;18:265-271.
16. Ruyter IE. Unpolymerized surface layers on sealants. Acta Odontol Scand 1981;39:27-32.
17. Rueggeberg FA, Margenson DH. The effect of oxygen inhibition on an unfilled/filled composite system. J Dent Res 1990;69:1652-1658.
18. Tay FR, Pashley DH. Aggressiveness of contemporary self-etching systems. I: Depth of penetration beyond dentin smear layers. Dent Mater 2001;17:296-308.
19. Sideridou I, Tserki V, Papanastasiou G. Effect of chemical structure on degree of conversion in light-cured dimethacrylate-based dental resins. Biomaterials 2002;23:1819-1829.
20. Pearson GJ, Longman CM. Water sorption and solubility of resin-based materials following inadequate polymerization by a visible-light curing system. J Oral Rehabil 1989;16:57-61.

LEGENDS:

Figure 1. FTIR spectrum sites obtained from Single Bond and Clearfil SE Bond adhesive resins before light exposure (segmented line), immediately after light exposure (α) and after 1 week (β). Little reduction in the peak located at 1638 cm^{-1} was observed immediately after light exposure (α) when Single Bond was light-cured with halogen light (A) or LED (B). FTIR analysis of Clearfil SE Bond exhibited similar reduction when halogen light was applied (C), while this reduction was less pronounced when LED was used (D). After 1 week, FTIR analysis of all samples exhibited a pronounced reduction in the same peak (β).

Figure 1

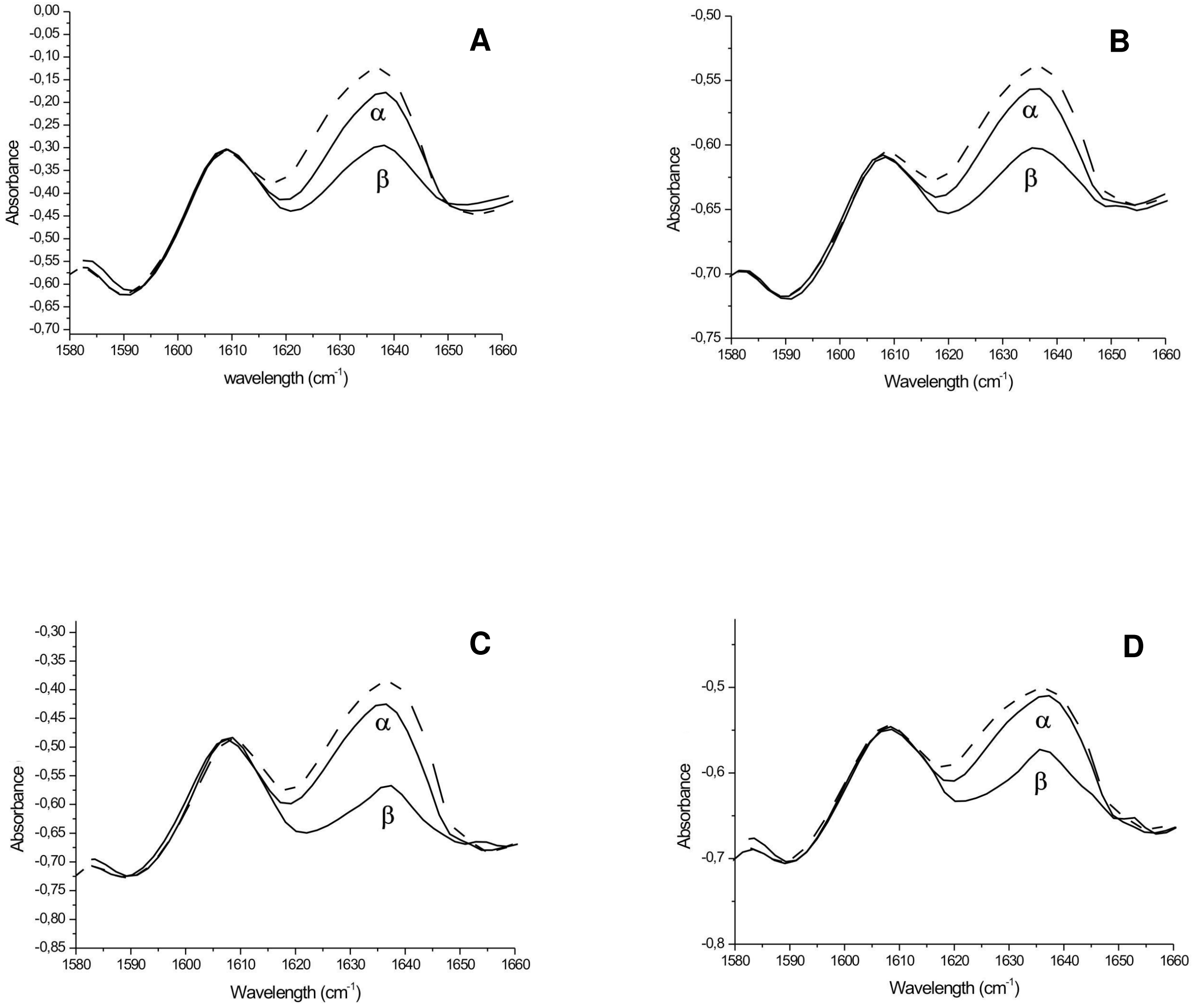

A
α
β
Absorbance
0,00
-0,05
-0,10
-0,15
-0,20
-0,25
-0,30
-0,35
-0,40
-0,45
-0,50
-0,55
-0,60
-0,65
-0,70
1580 1590 1600 1610 1620 1630 1640 1650 1660
wavelength (cm-1)
B
α
β
Absorbance
-0,50
-0,55
-0,60
-0,65
-0,70
-0,75
1580 1590 1600 1610 1620 1630 1640 1650 1660
Wavelength (cm-1)
C
α
β
Absorbance
-0,30
-0,35
-0,40
-0,45
-0,50
-0,55
-0,60
-0,65
-0,70
-0,75
-0,80
-0,85
1580 1590 1600 1610 1620 1630 1640 1650 1660
Wavelength (cm-1)
D
α
β
Absorbance
-0,5
-0,6
-0,7
-0,8
1580 1590 1600 1610 1620 1630 1640 1650 1660
Wavelength (cm-1)

Table 1. Composition of the adhesive systems used in this study.

Adhesive Systems	Composition	Lot Number
Single Bond	Bis-GMA, HEMA, UDMA, Bisphenol A glycerolate, PAA, dimethacrylate, water, ethanol.	3HR
Clearfil SE Bond	*SE-Primer*: MDP, HEMA, CQ, N,N -Diethanol p -toluidine, hydrophilic dimethacrylate and water. *SE-Bond*: MDP, Bis -GMA, HEMA, hydrophobic dimethacrylate, CQ, N,N -Diethanol p -toluidine and silanated colloidal silica.	315

HEMA: 2-hydroxyethyl methacrylate; PAA: polyalkenoic acid copolymer; Bis-GMA: bisphenol A glycidy l methacrylate; UDMA: urethane dimethacrylate; MDP: 10 -methacryloxydecyl-dihydrogen phosphate and CQ: camphorquinone.

Table 2. Specifications and technicality details of the light-curing units used in this study.

Curing Unit	Power Source	Ligth Type	Tip diameter (mm)	Light Source
XL-3000	Mains	Quartz tungsten halogen (QTH)	8	1 QTH bulb
Elipar Freelight 1	Battery	Light emitting diode (LED)	6	19 LED in an array

Table 3. Degree of conversion means (± standard deviation) for adhesive systems after photo-activation with halogen light (HAL) and light emitting diode (LED) -based curing units.

	Single Bond	Clearfil SE Bond
HAL	35.0 ± 5.2 A a	35.0 ± 2.4 A a
LED	32.0 ± 4.0 B a	27.7 ± 3.0 B b

Means followed by different letters (capital letter – column; lower case – row) differ statistically by Tukey test ($p < 0.05$).

Table 4. Single Bond degree of conversion (DC) means (± standard deviation) with halogen light (HAL) and light emitting diode (LED) curing units.

	DC immediately after curing	DC after 1 week
HAL	18.7 ± 3.9 A a	51.3 ± 6.6 A b
LED	13.5 ± 3.3 B a	50.3 ± 4.8 B b

Means followed by different letters (capital letter – column; lower case – row) differ statistically by Tukey test ($p < 0.05$).

Table 5. Clearfil SE Bond degree of conversion (DC) means (± standard deviation) with halogen light (HAL) and light emitting diode (LED) curing units.

	DC immediately after curing	DC after 1 week
HAL	13.6 ± 1.9 A a	56.5 ± 2.9 A b
LED	6.1 ± 1.0 B a	49.2 ± 4.9 B b

Means followed by different letters (capital letter – column; lower case – row) differ statistically by Tukey test ($p < 0.05$).

4. DISCUSSÃO GERAL

A todo instante tem-se buscado o desenvolvimento de técnicas restauradoras e materiais resinosos que proporcionem a formação de uma interface de união com melhores propriedades mecânicas e com alta durabilidade. A qualidade de infiltração, composição e grau de conversão dos monômeros resinosos infiltrados na dentina constituem alguns dos fatores primordiais para que tais propriedades apresentem as mínimas exigências para a criação de interfaces de união de restaurações diretas e indiretas confiáveis a curto e longo prazo (De Munck *et al.*, 2003; Erickson, 1992; Nakabayashi *et al.*, 1982). Neste contexto, agentes de união de dupla ativação foram desenvolvidos com o intuito de assegurar que adequado grau de conversão seja obtido na interface de união quando restaurações indiretas são confeccionadas, uma vez que tais sistemas adesivos poderiam assegurar que a reação de polimerização ocorresse mesmo quando a luz da unidade de fotoativação fosse extremamente atenuada pela presença da restauração indireta (Milleding *et al.*, 1995; Nathanson, 1987). Além disso, tais sistemas adesivos impedem que ocorra a incompatibilidade química com cimentos resinosos de dupla ativação previamente descrita na literatura (Mak *et al.*, 2002; Sanares *et al.*, 2001; Yamauchi, 1986).

O primeiro capítulo deste estudo foi voltado para a avaliação da efetividade de uma técnica alternativa de aplicação de sistemas de união de dupla ativação na cimentação de restaurações indiretas de compósito. Uma vez que estudos têm demonstrado que a fotoativação prévia dos agentes de união pode promover a desadaptação da restauração indireta (Frankenberger *et al.*, 1999; Hahn *et al.*, 2000; Pashley, 1991), este estudo avaliou a efetividade dos agentes de união de dupla ativação quando os mesmos não foram fotoativados previamente a aplicação do cimento resinoso e o assentamento da peça protética. A evidência de que os valores de união não foram afetados e que até aumentaram quando um dos sistemas de cimentação de dupla ativação não foi fotoativado permite a adoção desta técnica de cimentação de restaurações indiretas quando utilizados os materiais avaliados no Capítulo 1. No entanto, cabe salientar que tal procedimento só pode ser considerado confiável quando sistemas de união de dupla ativação são utilizados, uma vez que os mesmos apresentam alguns componentes como sulfinatos aromáticos de sódio que impedem que as aminas terciárias da reação peróxido-amina sejam neutralizadas, o que impediria que a reação de autopolimerização ocorresse (Sanares *et al.*, 2001; Yamauchi, 1986). Considerando-se que outros sistemas adesivos de dupla ativação contêm componentes diferentes dos sulfinatos aromáticos de sódio como peróxido de benzoíla e outras aminas aromáticas, torna-se necessária a avaliação desses outros sistemas para validação desta técnica de fixação adesiva de restaurações indiretas.

A análise da morfologia da interface de união utilizando-se microscopia confocal laser forneceu evidências que podem justificar as diferenças observadas na resistência de união quando All Bond 2 foi utilizado, em que valores de união foram superiores quando o primer não foi fotoativado. De acordo com as imagens exibidas no Capítulo 2, foi possível observar que a resina adesiva Pre-Bond pôde penetrar no interior dos túbulos dentinários bem como também em parte da camada híbrida. Composto principalmente por monômeros hidrófobos de longa cadeia e sem solventes, a resina Pre-Bond aparentemente alterou a composição da resina adesiva no interior da camada híbrida, resultando em um polímero com propriedades mecânicas melhoradas. Devido provavelmente à viscosidade da resina Pre-Bond aplicada previamente à aplicação do cimento resinoso Duolink, não foi observada a penetração do cimento no interior da camada híbrida, mas apenas na entrada dos túbulos dentinários.

Quando o sistema adesivo de dupla ativação de quinta geração Bond 1 (adesivo de frasco único com condicionamento com ácido fosfórico separadamente) foi utilizado, foi possível notar a penetração de componentes do cimento resinoso de dupla ativação (Lute-it) no interior da camada híbrida e nos túbulos dentinários. Esta penetração mostrou-se mais acentuada quando os sistemas não foram fotoativados e deste modo a lenta reação de autopolimerização permitiu maior difusão do cimento no interior da dentina. O aumento da concentração de Bis-GMA e outros monômeros hidrófobos da resina adesiva Pre-Bond para All Bond 2 ou mesmo do cimento resinoso para Bond 1 no interior da camada híbrida pode reduzir o grau de solubilidade do polímero infiltrado na dentina desmineralizada como descrito previamente por Asmussen & Uno (1993). Como conseqüência, uma interface de união mais resistente à degradação pode ter sido formada e deste modo maior durabilidade da interface de união pode ser esperada. No entanto, apenas estudos envolvendo a análise de resistência à tração da interface de união após armazenamento de dentes restaurados indiretamente pode confirmar tal hipótese.

Na intenção de se averiguar a efetividade dos sistemas adesivos de dupla ativação, a análise do grau de conversão foi realizada através da simulação da fixação de restaurações indiretas utilizando-se os agentes de união, os respectivos cimentos resinosos e discos pré-polimerizados de compósito, os quais simularam a restauração protética. Simulações das mais severas condições clínicas em que a luz fotoativadora é extremamente atenuada ou até mesmo ausente foram também realizadas como descrito no Capítulo 3. Através deste método de análise, foi possível verificar que todos os sistemas de cimentação apresentaram adequada reação de polimerização mesmo nas condições em que fotoativação não foi realizada. As diferenças no grau de conversão podem ser atribuídas às próprias limitações da reação de autopolimerização, como baixa cinética de reação e alta viscosidade atribuída aos cimentos resinosos como previamente demonstrado (Rueggeberg & Caughman, 1993). Estudos pilotos realizados utilizando o mesmo método de análise do grau de conversão da interface de união de restaurações indiretas de compósito mas com a utilização de sistemas adesivos de quinta geração convencionais, ou seja, sem co-iniciadores, demonstrou que a presença dos adesivos foi suficiente para inibir a reação de autopolimerização da superfície de cimento resinoso em contato com a resina adesiva. Este achado corrobora com os resultados de outros autores que observaram baixa resistência de união quando compósitos autopolimerizáveis eram aplicados sobre resinas adesivas com baixo pH (Sanares *et al.*, 2001; Suh *et al.*, 2003) e denota a importância da utilização sistemas adesivos de dupla ativação na fixação de restaurações indiretas. A utilização deste tipo de agente de união se faz necessária mesmo quando a camada de resina adesiva for polimerizada previamente à aplicação do cimento resinoso, considerando-se que mesmo nestas condições haverá a camada de adesivo não polimerizada devido à presença de oxigênio, camada esta capaz de interagir com o cimento resinoso e impedir a reação de autopolimerização quando a luz fotoativadora for insuficiente ou ausente devido à presença da restauração indireta (Rueggeberg & Margeson, 1990; Ruyter, 1981).

Os resultados do grau de conversão observados no Capítulo 3 correspondem ao grau de conversão da camada combinada criada, composta por resina adesiva e cimento resinoso. Desta forma, os resultados aqui demonstrados podem representar o grau de conversão de diferentes regiões da interface de união, os quais podem variar de acordo com o sistema de cimentação utilizado. Em outras palavras, no caso de sistemas de cimentação em que a penetração do cimento resinoso restringe-se apenas à entrada dos túbulos, os resultados observados neste capítulo correspondem ao grau de conversão da camada adesiva localizada na superfície dentinária e na entrada dos túbulos. Neste caso, estudos adicionais envolvendo a análise do grau de conversão de adesivos dentinários de dupla ativação em diferentes condições de ativação sem a presença do cimento resinoso são fundamentais para o melhor entendimento sobre a polimerização destes monômeros na camada híbrida quando a fotoativação é comprometida. Por outro lado, quando o cimento resinoso penetrou não só no interior dos túbulos dentinários como também no interior da camada híbrida, como observado para o adesivo de quinta geração no Capítulo 2, os valores de grau de conversão observados no Capítulo 3 podem corresponder ao grau de conversão do sistema no interior da camada híbrida.

No intuito de se verificar as propriedades mecânicas da interface de união de restaurações indiretas quando a resina de união não foi fotoativada e a restauração foi fotoativada ou não, diferentes sistemas foram avaliados, entre eles sistemas de cimentação adesiva de quarta e quinta gerações, como descrito no Capítulo 4. Embora a maioria dos sistemas de cimentação de dupla ativação não tenha mostrado acentuada diferença no grau de conversão quando autopolimerizados como exposto no Capítulo 3, os valores de união da maioria dos sistemas foram consideravelmente baixos em um sistema de quarta geração e em um de quinta. A evidência de que os valores de união não estão relacionados ao grau de conversão poderia ser explicada por diferenças no modo de penetração do cimento resinoso no interior da camada híbrida. No entanto, como se pôde observar nos Capítulos 2 e 4, o sistema de cimentação de dupla ativação Bond 1 / Lute-it apresentou elevado grau de conversão e penetração do cimento resinoso no interior dos túbulos dentinários e na camada híbrida, porém apresentou baixos valores de união quando o sistema não foi fotoativado. Os agentes de união de quinta geração são aplicados em dentina úmida e os monômeros misturam-se com a água residual do substrato dentinário no momento da polimerização (Jacobsen & Soderholm, 1995). Como previamente demonstrado (Asmussen, 1981; Lee & Um, 2001) e também observado no Capítulo 4, a cinética de reação dos sistemas de cimentação para autopolimerização mostrou-se consideravelmente lenta em comparação com aquela observada quando os sistemas foram fotoativadas. Provavelmente por esta razão, Tanoue *et al.* (2003) observou que cimentos resinosos de dupla ativação apresentavam maior solubilidade e sorpção de água quando autopolimerizados. Deste modo, é possível que a presença de água tenha levado à formação polimérica deficiente no interior da camada híbrida quando o sistema de cimentação foi autopolimerizado.

Curiosamente, o sistema de cimentação de dupla ativação All Bond 2 / Duolink exibiu as maiores diferenças quando comparados os valores de grau de conversão do sistema fotoativado com os valores de grau de conversão do sistema autopolimerizado, porém foi o único sistema de cimentação que não demonstrou diferença significante nos valores de união quando o modo autopolimerizável foi comparado ao fotopolimerizável. Como descrito no Capítulo

4, o padrão de fratura predominante observado para All Bond 2 / Duolink foi basicamente localizado na região de camada híbrida, onde não houve penetração do cimento resinoso. Desta forma, pode-se especular que a resistência de união neste caso dependeu principalmente da capacidade de autopolimerização do agente de união sem a presença do cimento resinoso após 24 horas, tempo de armazenamento aguardado previamente à realização do ensaio mecânico.

A utilização de diferentes tipos de unidades fotoativadoras pode comprometer ainda mais a efetividade dos sistemas de cimentação de dupla ativação, uma vez que a baixa intensidade de luz de alguns deles pode promover baixo grau de conversão de materiais resinosos logo após fotoativação, como demonstrado no Capítulo 5. Entretanto, independentemente da unidade de fotoativação utilizada, baixos valores de grau de conversão foram observados imediatamente após a fotoativação para os produtos avaliados. Tal evidência pode ser atribuída aos efeitos da presença de oxigênio na fina camada de adesivo e conseqüentemente à formação da camada de adesivo com polimerização inibida pelo oxigênio (Rueggeberg & Margeson, 1990; Ruyter, 1981), bem como pelo pouco tempo de fotoativação (10 segundos) e de reação entre o momento da fotoativação e a realização da análise do espécime através da Espectroscopia Infravermelha Transformada de Fourier. Considerando-se que a espessura da camada de adesivo não polimerizada devido à presença de oxigênio depende da viscosidade do material e da intensidade da luz fotoativadora (Ruyter, 1981), é provável que sistemas de união que apresentam baixa viscosidade como alguns de quinta geração possam apresentar camada não polimerizada estendida até o interior da camada híbrida. Esta hipótese pode constituir uma das razões para a penetração de componentes do cimento resinoso no topo da camada híbrida mesmo quando a resina de união foi fotoativada previamente à aplicação do cimento resinoso, como observado no Capítulo 2.

A unidade de fotoativação LED utilizada no estudo descrito no Capítulo 5 pertence a primeira geração de LEDs, apresentando densidade de luz em torno de 400 mW/cm^2, de acordo com o fabricante. Como demonstrado no Capítulo 4, dependendo da cor da restauração indireta, apenas 10% da densidade de luz de uma unidade de fotoativação atinge o cimento resinoso abaixo da restauração. Como conseqüência, apenas aproximadamente 40 mW/cm^2 de luz emitida pelo LED iniciaria a polimerização do cimento resinoso e menor densidade de luz atingiria o agente de união quando comparada à obtida com a utilização da luz halógena. Deste modo, em comparação ao grau de conversão observado no Capítulo 4 quando restaurações indiretas de diferentes cores impediam a completa passagem da luz fotoativadora, menores valores de grau de conversão podem ser esperados de sistemas de cimentação de dupla ativação quando LED é utilizado.

Com base nos resultados aqui observados, cuidados devem ser tomados no momento da seleção e da técnica de cimentação dos sistemas de dupla ativação para que adequada polimerização e propriedades mecânicas sejam alcançadas, as quais dependerão de algumas condições clínicas, como possibilidade de fotoativação com densidade de luz mínima para o início da reação de polimerização, uma vez que a reação de autopolimerização ainda não proporciona resistência de união aceitável para diversos sistemas de cimentação de dupla polimerização. Considerando-se as vantagens que oferece, a técnica de cimentação de restaurações indiretas em que a camada do sistema adesivo não é fotoativada previamente à aplicação do cimento resinoso pode ser considerada uma opção aceitável do ponto de vista clínico desde que os sistemas de união sejam de dupla ativação para eliminar a incompatibilidade entre as resinas de união e os cimentos resinosos de dupla ativação. No entanto, estudos adicionais envolvendo a análise em longo prazo dos efeitos desta técnica de cimentação são fundamentais para melhor compreensão da combinação entre agentes de união não polimerizados e cimentos resinosos.

5. CONCLUSÕES GERAIS:

De acordo com os resultados obtidos nos diferentes estudos realizados, pode-se concluir que:

1. A resistência à tração de sistemas de cimentação de dupla ativação quando os agentes de união de dupla ativação deixados na forma não polimerizada previamente à aplicação dos cimentos não foi reduzida em comparação aos valores obtidos quando os agentes de união foram fotoativados. Para um sistema de cimentação, os valores de união foram superiores quando os agentes de união de dupla ativação foram deixados na forma não polimerizada.

2. As análises de microscopia confocal laser e eletrônica de varredura demonstraram diferentes morfologias de interface de união, as quais variaram de acordo com os sistemas de cimentação e com os modos de ativação dos agentes de união e dos cimentos resinosos avaliados.

3. Os resultados de grau de conversão dos sistemas de cimentação de dupla ativação avaliados demonstraram que o uso de diferentes valores da cor A em restaurações indiretas de compósito posicionadas entre a luz fotoativadora e os sistemas reduziu o grau de conversão para a maioria dos sistemas e o modo autopolimerizável não atingiu os valores obtidos quando os sistemas foram diretamente expostos à luz fotoativadora.

4. A autopolimerização dos sistemas de cimentação reduziu as propriedades mecânicas da maioria dos sistemas de cimentação de dupla ativação em comparação com a fotoativação. Apenas um sistema de cimentação não apresentou diferenças significantes nos valores de união quando comparados os dois modos de ativação.

5. A fotoativação com LED promoveu valores de grau de conversão inferiores aos obtidos quando luz halógena foi utilizada, tanto imediatamente quanto uma semana após a fotoativação.

6. Referências Bibliográficas:

Asmussen E. Setting time of composite restorative resins vs. content of amine, peroxide, and inhibitor. ***Acta Odontol Scand.*** 1981; 39(5): 291-4.

Asmussen E, Uno S. Solubility parameters, fractional polarities, and bond strengths of some intermediary resins used in dentin bonding. ***J Dent Res.*** 1993; 72(3): 558-65.

D'Alpino PH, Pereira JC, Rueggeberg FA, Svizero NR, Miyake K, Pashley DH. Efficacy of composite surface sealers in sealing cavosurface marginal gaps. ***J Dent.*** 2006a; 34(3): 252-9.

D'Alpino PH, Pereira JC, Svizero NR, Rueggeberg FA, Pashley DH. Use of fluorescent compounds in assessing bonded resin-based restorations: A literature review. ***J Dent.*** 2006b; 34(9): 623-4.

De Munck J, Van Meerbeek B, Yoshida Y, Inoue S, Vargas M, Suzuki K *et al.* Four-year water degradation of total-etch adhesives bonded to dentin. ***J Dent Res.*** 2003; 82(2): 136-40.

Dietschi D, Herzfeld D. In vitro evaluation of marginal and internal adaptation of class II resin composite restorations after thermal and occlusal stressing. ***Eur J Oral Sci.*** 1998; 106(6): 1033-42.

Erickson RL. Surface interactions of dentin adhesive materials. ***Oper Dent.*** 1992; Suppl 5: 81-94.

Frankenberger R, Sindel J, Kramer N, Petschelt A. Dentin bond strength and marginal adaptation: direct composite resins vs ceramic inlays. ***Oper Dent.*** 1999; 24(3): 147-55.

Fujibayashi K, Ishimaru K, Kohno A. Newly developed light-activation units using blue light-emitting diodes. ***Jpn J Consev Dent.*** 1996; 39: 180-8.

Giannini M, De Goes MF, Nikaido T, Shimada Y, Tagami J. Influence of activation mode of dual-cured resin composite cores and low-viscosity composite liners on bond strength to dentin treated with self-etching adhesives. ***J Adhes Dent.*** 2004; 6(4): 301-6.

Hahn P, Schaller H, Hafner P, Hellwig E. Effect of different luting procedures on the seating of ceramic inlays. ***J Oral Rehabil.*** 2000; 27(1): 1-8.

Ikemura K, Endo K. Effect of adhesion of new polymerization initiator systems comprising 5-monosubstituted barbituric acids, aromatic sulfinate amides, and ter-butyl peroxymaleic acid in dental adhesive resin. ***J Appl Polym Sci.*** 1999; 72: 1655-68.

Inokoshi S, Willems G, Van Meerbeek B, Lambrechts P, Braem M, Vanherle G. Dual-cure luting composites: Part I: Filler particle distribution. ***J Oral Rehabil.*** 1993; 20(2): 133-46.

Jacobsen T, Soderholm KJ. Some effects of water on dentin bonding. ***Dent Mater.*** 1995; 11(2): 132-6.

Knezevic A, Tarle Z, Meniga A, Sutalo J, Pichler G, Ristic M. Degree of conversion and temperature rise during polymerization of composite resin samples with blue diodes. ***J Oral Rehabil.*** 2001; 28(6): 586-91.

Lee IB, Um CM. Thermal analysis on the cure speed of dual cured resin cements under porcelain inlays. ***J Oral Rehabil.*** 2001; 28(2): 186-97.

Leinfelder KF. Indirect posterior composite resins. ***Compend Contin Educ Dent.*** 2005; 26(7): 495-503; quiz 4, 27.

Magne P, Douglas WH. Porcelain veneers: dentin bonding optimization and biomimetic recovery of the crown. ***Int J Prosthodont.*** 1999; 12(2): 111-21.

Mak YF, Lai SC, Cheung GS, Chan AW, Tay FR, Pashley DH. Micro-tensile bond testing of resin cements to dentin and an indirect resin composite. ***Dent Mater.*** 2002; 18(8): 609-21.

Manhart J, Chen H, Hamm G, Hickel R. Buonocore Memorial Lecture. Review of the clinical survival of direct and indirect restorations in posterior teeth of the permanent dentition. ***Oper Dent.*** 2004; 29(5): 481-508.

McCabe JF, Rusby S. Dentine bonding--the effect of pre-curing the bonding resin. ***Br Dent J.*** 1994; 176(9): 333-6.

Milleding P. Microleakage of indirect composite inlays. An in vitro comparison with the direct technique. ***Acta Odontol Scand.*** 1992; 50(5): 295-301.

Milleding P, Ortengren U, Karlsson S. Ceramic inlay systems: some clinical aspects. ***J Oral Rehabil.*** 1995; 22(8): 571-80.

Nakabayashi N, Kojima K, Masuhara E. The promotion of adhesion by the infiltration of monomers into tooth substrates. ***J Biomed Mater Res.*** 1982; 16(3): 265-73.

Nathanson D. Etched porcelain restorations for improved esthetics, part II: Onlays. ***Compendium.*** 1987; 8(2): 105-10.

Nomura Y, Teshima W, Tanaka N, Yoshida Y, Nahara Y, Okazaki M. Thermal analysis of dental resins cured with blue light-emitting diodes (LEDs). ***J Biomed Mater Res.*** 2002; 63(2): 209-13.

Pashley DH. In vitro simulations of in vivo bonding conditions. ***Am J Dent.*** 1991; 4(5): 237-40.

Raigrodski AJ. All-ceramic full-coverage restorations: concepts and guidelines for material selection. ***Pract Proced Aesthet Dent.*** 2005; 17(4): 249-56; quiz 58.

Rasetto FH, Driscoll CF, Prestipino V, Masri R, von Fraunhofer JA. Light transmission through all-ceramic dental materials: a pilot study. ***J Prosthet Dent.*** 2004; 91(5): 441-6.

Rueggeberg FA, Hashinger DT, Fairhurst CW. Calibration of FTIR conversion analysis of contemporary dental resin composites. ***Dent Mater.*** 1990; 6(4): 241-9.

Rueggeberg FA, Margeson DH. The effect of oxygen inhibition on an unfilled/filled composite system. ***J Dent Res.*** 1990; 69(10): 1652-8.

Rueggeberg FA, Caughman WF. The influence of light exposure on polymerization of dual-cure resin cements. ***Oper Dent.*** 1993; 18(2): 48-55.

Ruyter IE, Svendsen SA. Remaining methacrylate groups in composite restorative materials. ***Acta Odontol Scand.*** 1978; 36(2): 75-82.

Ruyter IE. Unpolymerized surface layers on sealants. ***Acta Odontol Scand.*** 1981; 39(1): 27-32.

Ruyter IE, Oysaed H. Conversion in denture base polymers. ***J Biomed Mater Res.*** 1982; 16(5): 741-54.

Sanares AM, Itthagarun A, King NM, Tay FR, Pashley DH. Adverse surface interactions between one-bottle light-cured adhesives and chemical-cured composites. ***Dent Mater.*** 2001; 17(6): 542-56.

Sjogren G, Molin M, van Dijken J, Bergman M. Ceramic inlays (Cerec) cemented with either a dual-cured or a chemically cured composite resin luting agent. A 2-year clinical study. ***Acta Odontol Scand.*** 1995; 53(5): 325-30.

Strang R, McCrosson J, Muirhead GM, Richardson SA. The setting of visible-light-cured resins beneath etched porcelain veneers. ***Br Dent J.*** 1987; 163(5): 149-51.

Suh BI, Feng L, Pashley DH, Tay FR. Factors contributing to the incompatibility between simplified-step adhesives and chemically-cured or dual-cured composites. Part III. Effect of acidic resin monomers. ***J Adhes Dent.*** 2003; 5(4): 267-82.

Tanaka J, Ishikawa K, Yatani H, Yamashita A, Suzuki K. Correlation of dentin bond durability with water absorption of bonding layer. ***Dent Mater J.*** 1999; 18(1): 11-8.

Tanoue N, Koishi Y, Atsuta M, Matsumura H. Properties of dual-curable luting composites polymerized with single and dual curing modes. ***J Oral Rehabil.*** 2003; 30(10): 1015-21.

Tay FR, Suh BI, Pashley DH, Prati C, Chuang SF, Li F. Factors contributing to the incompatibility between simplified-step adhesives and self-cured or dual-cured composites. Part II. Single-bottle, total-etch adhesive. ***J Adhes Dent.*** 2003; 5(2): 91-105.

van Dijken JW. A 6-year evaluation of a direct composite resin inlay/onlay system and glass ionomer cement-composite resin sandwich restorations. ***Acta Odontol Scand.*** 1994; 52(6): 368-76.

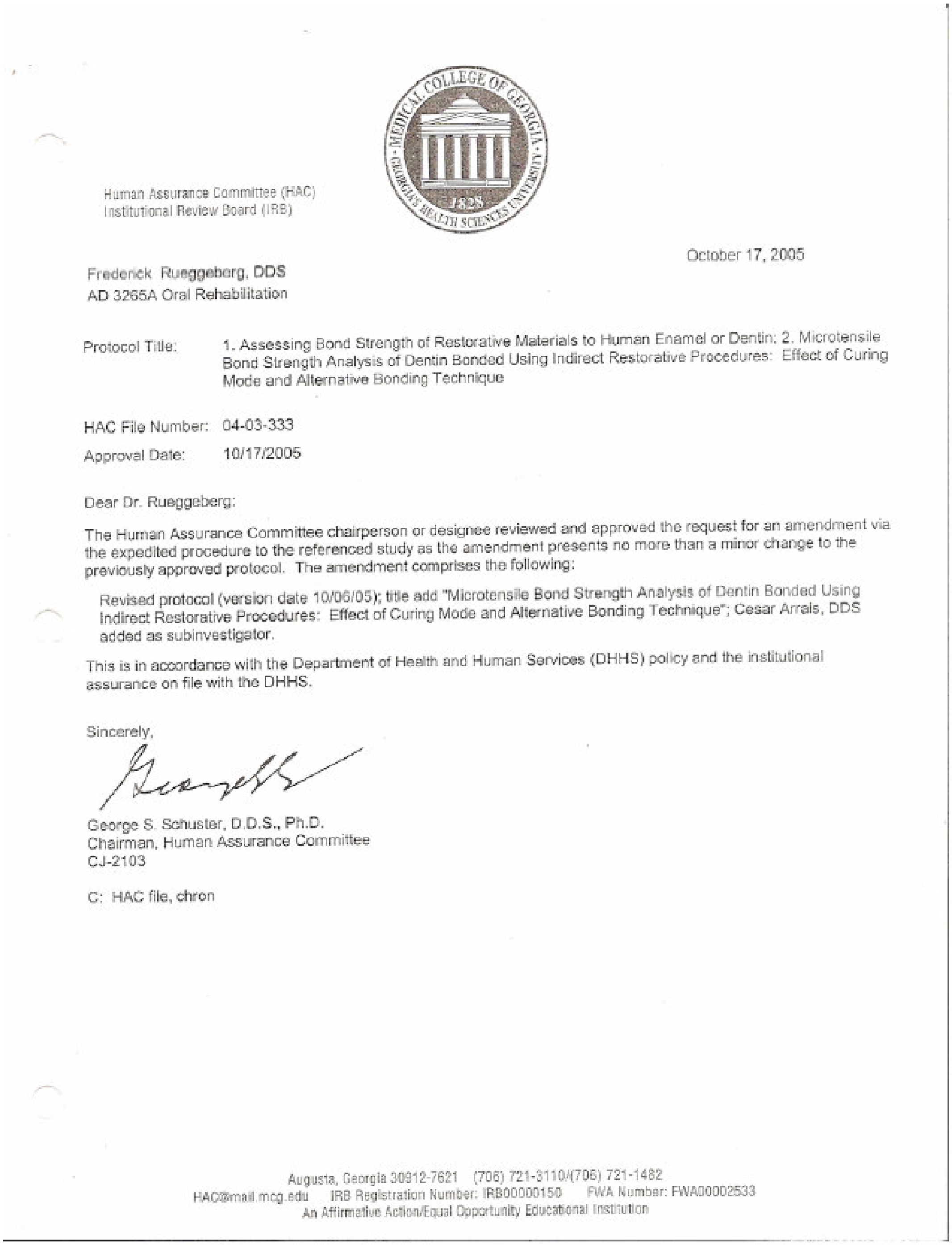
Versluis A, Tantbirojn D, Douglas WH. Distribution of transient properties during polymerization of a light-initiated restorative composite. ***Dent Mater.*** 2004; 20(6): 543-53.

Wang SF, Chuang CP, Lee WH. Free radical reaction of - allyl-sulfonylalkyl substituted aromatic derivatives. ***Tetrahedron.*** 1999; 55: 6109-18.

Yamauchi J. Study of dental adhesive containning phosphoric acid methacrylate monomer. ***Japanese Journal of Dental Materials.*** 1986; 5: 144-54.

7. Anexos:

7.1. ANEXO: Documento de certificação da aprovação do Comitê de Ética para a utilização de dentes humanos nos Capítulos 1, 2 e 4.



MEDICAL COLLEGE OF GEORGIA
1828

Human Assurance Committee (HAC)
Institutional Review Board (IRB)

October 17, 2005

Frederick Rueggeberg, DDS
AD 3265A Oral Rehabilitation

Protocol Title: 1. Assessing Bond Strength of Restorative Materials to Human Enamel or Dentin; 2. Microtensile Bond Strength Analysis of Dentin Bonded Using Indirect Restorative Procedures: Effect of Curing Mode and Alternative Bonding Technique

HAC File Number: 04-03-333

Approval Date: 10/17/2005

Dear Dr. Rueggeberg:

The Human Assurance Committee chairperson or designee reviewed and approved the request for an amendment via the expedited procedure to the referenced study as the amendment presents no more than a minor change to the previously approved protocol. The amendment comprises the following:

Revised protocol (version date 10/06/05); title add "Microtensile Bond Strength Analysis of Dentin Bonded Using Indirect Restorative Procedures: Effect of Curing Mode and Alternative Bonding Technique"; Cesar Arrais, DDS added as subinvestigator.

This is in accordance with the Department of Health and Human Services (DHHS) policy and the institutional assurance on file with the DHHS.

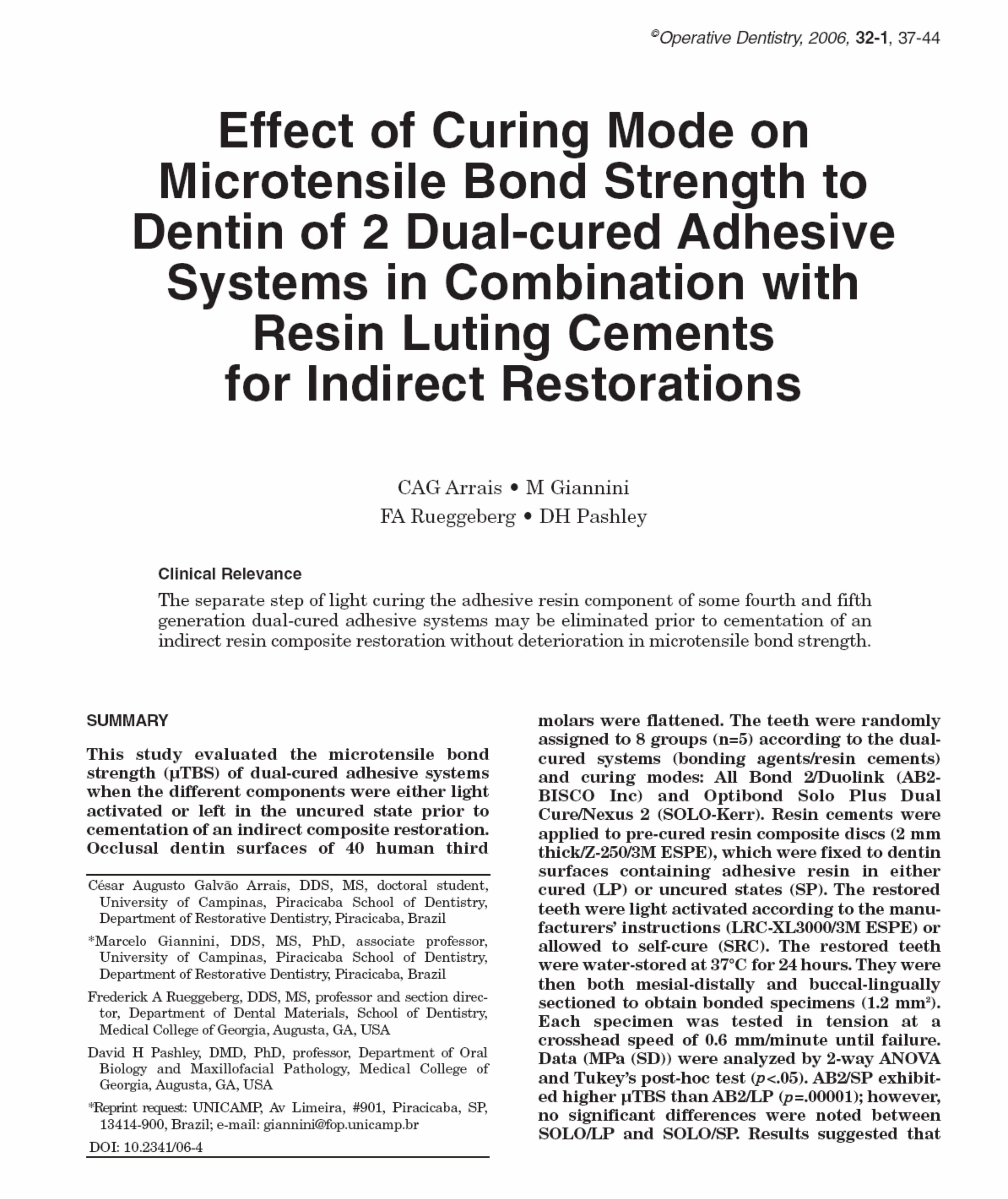
Sincerely,

George S. Schuster, D.D.S., Ph.D.
Chairman, Human Assurance Committee
CJ-2103

C: HAC file, chron

Augusta, Georgia 30912-7621 (706) 721-3110/(706) 721-1482
HAC@mail.mcg.edu IRB Registration Number: IRB00000150 FWA Number: FWA00002533
An Affirmative Action/Equal Opportunity Educational Institution

7.2. ANEXO: Primeira página do artigo referente ao Capítulo 1



©*Operative Dentistry, 2006,* **32-1**, 37-44

Effect of Curing Mode on Microtensile Bond Strength to Dentin of 2 Dual-cured Adhesive Systems in Combination with Resin Luting Cements for Indirect Restorations

CAG Arrais • M Giannini
FA Rueggeberg • DH Pashley

Clinical Relevance

The separate step of light curing the adhesive resin component of some fourth and fifth generation dual-cured adhesive systems may be eliminated prior to cementation of an indirect resin composite restoration without deterioration in microtensile bond strength.

SUMMARY

This study evaluated the microtensile bond strength (μTBS) of dual-cured adhesive systems when the different components were either light activated or left in the uncured state prior to cementation of an indirect composite restoration. Occlusal dentin surfaces of 40 human third molars were flattened. The teeth were randomly assigned to 8 groups (n=5) according to the dual-cured systems (bonding agents/resin cements) and curing modes: All Bond 2/Duolink (AB2-BISCO Inc) and Optibond Solo Plus Dual Cure/Nexus 2 (SOLO-Kerr). Resin cements were applied to pre-cured resin composite discs (2 mm thick/Z-250/3M ESPE), which were fixed to dentin surfaces containing adhesive resin in either cured (LP) or uncured states (SP). The restored teeth were light activated according to the manufacturers' instructions (LRC-XL3000/3M ESPE) or allowed to self-cure (SRC). The restored teeth were water-stored at 37°C for 24 hours. They were then both mesial-distally and buccal-lingually sectioned to obtain bonded specimens (1.2 mm²). Each specimen was tested in tension at a crosshead speed of 0.6 mm/minute until failure. Data (MPa (SD)) were analyzed by 2-way ANOVA and Tukey's post-hoc test ($p<.05$). AB2/SP exhibited higher μTBS than AB2/LP ($p=.00001$); however, no significant differences were noted between SOLO/LP and SOLO/SP. Results suggested that

---

César Augusto Galvão Arrais, DDS, MS, doctoral student, University of Campinas, Piracicaba School of Dentistry, Department of Restorative Dentistry, Piracicaba, Brazil

*Marcelo Giannini, DDS, MS, PhD, associate professor, University of Campinas, Piracicaba School of Dentistry, Department of Restorative Dentistry, Piracicaba, Brazil

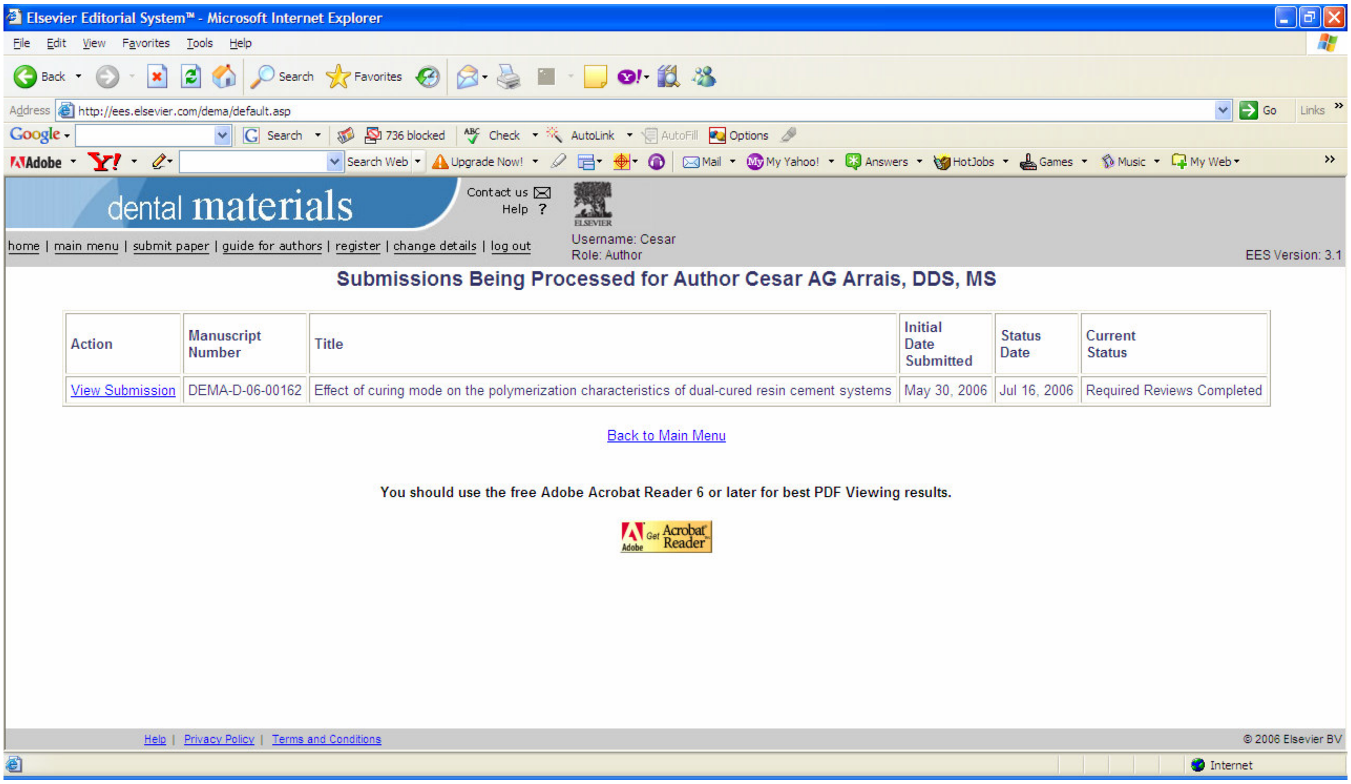
Frederick A Rueggeberg, DDS, MS, professor and section director, Department of Dental Materials, School of Dentistry, Medical College of Georgia, Augusta, GA, USA

David H Pashley, DMD, PhD, professor, Department of Oral Biology and Maxillofacial Pathology, Medical College of Georgia, Augusta, GA, USA

*Reprint request: UNICAMP, Av Limeira, #901, Piracicaba, SP, 13414-900, Brazil; e-mail: giannini@fop.unicamp.br

DOI: 10.2341/06-4

7.3. ANEXO 2: Documento para comprovação da submissão para publicação do artigo referente ao capítulo 3



http://ees.elsevier.com/dema/default.asp

Username: Cesar
Role: Author

EES Version: 3.1

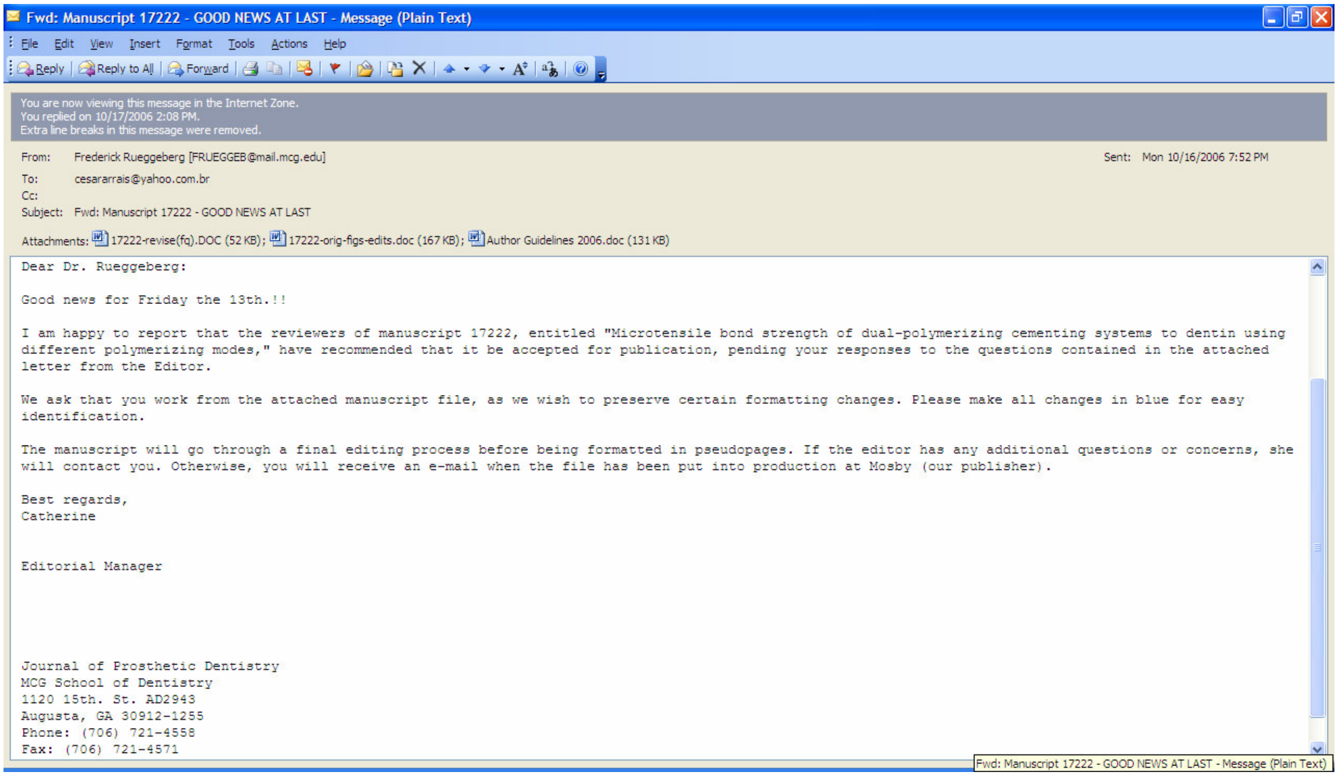
Submissions Being Processed for Author Cesar AG Arrais, DDS, MS

Action	Manuscript Number	Title	Initial Date Submitted	Status Date	Current Status
View Submission	DEMA-D-06-00162	Effect of curing mode on the polymerization characteristics of dual-cured resin cement systems	May 30, 2006	Jul 16, 2006	Required Reviews Completed

Back to Main Menu

You should use the free Adobe Acrobat Reader 6 or later for best PDF Viewing results.

7.4. ANEXO 3: Carta de aceitação do artigo referente ao Capítulo 4



You are now viewing this message in the Internet Zone.
You replied on 10/17/2006 2:08 PM.
Extra line breaks in this message were removed.

From: Frederick Rueggeberg [FRUEGGEB@mail.mcg.edu]
Sent: Mon 10/16/2006 7:52 PM
To: cesararrais@yahoo.com.br
Cc:
Subject: Fwd: Manuscript 17222 - GOOD NEWS AT LAST

Attachments: 17222-revise(fq).DOC (52 KB); 17222-orig-figs-edits.doc (167 KB); Author Guidelines 2006.doc (131 KB)

Dear Dr. Rueggeberg:

Good news for Friday the 13th.!!

I am happy to report that the reviewers of manuscript 17222, entitled "Microtensile bond strength of dual-polymerizing cementing systems to dentin using different polymerizing modes," have recommended that it be accepted for publication, pending your responses to the questions contained in the attached letter from the Editor.

We ask that you work from the attached manuscript file, as we wish to preserve certain formatting changes. Please make all changes in blue for easy identification.

The manuscript will go through a final editing process before being formatted in pseudopages. If the editor has any additional questions or concerns, she will contact you. Otherwise, you will receive an e-mail when the file has been put into production at Mosby (our publisher).

Best regards,
Catherine

Editorial Manager

Journal of Prosthetic Dentistry
MCG School of Dentistry
1120 15th. St. AD2943
Augusta, GA 30912-1255
Phone: (706) 721-4558
Fax: (706) 721-4571

7.5. ANEXO 4: Carta de aceitação do artigo referente ao Capítulo 5

Universidade de São Paulo
Faculdade de Odontologia de Ribeirão Preto
BRAZILIAN DENTAL JOURNAL
e-mails: bdj@forp.usp.br ou pecora@forp.usp.br
homepage: http://www.forp.usp.br/bdj
Avenida do Café s/n 14040-904 Ribeirão Preto, SP, Brasil. Fax 55-16-3633-0999

Ribeirão Preto, 04 de setembro de 2006.

Prezado Professor,

O trabalho BDJ 783 "**DEGREE OF CONVERSION OF ADHESIVE SYSTEMS LIGHT-CURED BY LED AND HALOGEN LIGHT** " .dos autores Cesar Augusto Galvão ARRAIS, Fenelon Martinho PONTES, Luis Presley Serejo dos SANTOS, Edson Roberto LEITE, Marcelo GIANNINI, foi aceito no mérito científico para publicação.

Contudo, devem-se ressaltar alguns aspectos que precedem à publicação do trabalho.

O artigo será submetido à apreciação do *Text & Technical Editor*, após o que, poderão ser necessárias alterações no conteúdo ou formatação do artigo, sem que isso implique na sua recusa. Os custos da revisão técnica (revisão do Inglês, correção formal do artigo e adequação às normas de publicação do BDJ) serão repassados aos autores.

Ademais, devido ao grande número de trabalhos já aprovados pelo Corpo Editorial ou em fase de avaliação, a publicação deste artigo não se dará antes de 18 meses, o que pode deixar de interessar a Vossa Senhoria. Dessa forma, aguardamos vossa manifestação quanto ao interesse na publicação.

Atenciosamente,

Prof. Dr. Manoel D. Sousa Neto ***Prof. Dr. Jesus Djalma***
Pécora
Editor ***Editor***

CASO SEU TRABALHO CONTENHA FIGURA(S), VERIFIQUE AS INFORMAÇOES DO QUADRO ABAIXO
Para a diagramação do artigo, é necessário que a(s) figura(s) esteja(m) no formato correto. **Figuras inseridas ou coladas em arquivos de programas como <u>WORD E POWER POINT NÃO SÃO ACEITAS</u>. Somente figuras em <u>PRETO E BRANCO</u> serão publicadas.** As imagens podem ser encaminhadas de duas maneiras: 1) Por correio: as figuras devem estar nítidas, impressas em papel fotográfico de boa qualidade (impressão em 300 dpi). Enviar para o seguinte endereço: Brazilian Dental Journal, Fundação Odontológica de Ribeirão Preto, A/C PAULO MARCOS FAZZIO, ASSUNTO: FIGURAS BDJ ____, Av. do Café, s/n 14040-904 Ribeirão Preto, SP, Brasil. 2) Por e-mail (bdj@forp.usp.br): as figuras devem ser geradas com resolução de 300 dpi. Encaminhar a(s) figura(s) como anexo(s), escrevendo no Assunto "Figuras referentes ao BDJ _________(no. do trabalho)". **OBSERVAÇÃO: O não envio das imagens ou o envio de imagens com baixa qualidade, implicará na solicitação de re-envio e, consequentemente, no atraso da publicação do trabalho**. **Em caso de dúvida sobre a adequação das figuras já enviadas quando da submissão do artigo, por favor, entre em contato.**

7.6. ANEXO 5: Declaração de responsabilidade pelos direitos autorais

UNIVERSIDADE ESTADUAL DE CAMPINAS
FACULDADE DE ODONTOLOGIA DE PIRACICABA

UNICAMP

DECLARAÇÃO

As cópias de artigos de minha autoria ou de minha co-autoria, já publicados ou submetidos para publicação em revistas científicas ou anais de congressos sujeitos a arbitragem, que constam da minha Dissertação/Tese de Doutorado, intitulada "INFLUÊNCIA DOS MODOS DE ATIVAÇÃO NO GRAU DE CONVERSÃO, RESISTÊNCIA E MORFOLOGIA DA INTERFACE DE UNIÃO DE SISTEMAS DE CIMENTAÇÃO E ADESIVOS", não infringem os dispositivos da Lei nº 9.610/98, nem o direito autoral de qualquer editora.

Piracicaba, 6 de novembro de 2006.

Cesar Augusto Galvão Arrais
RG Nº 116925115
AUTOR

Marcelo Giannini
RG Nº 18025770
ORIENTADOR