UNIVERSIDADE FEDERAL DE PELOTAS

Programa de Pós-graduação em Odontologia

Tese de Doutorado

Uso do hexafluorfosfato de difeniliodônio na polimerização radicalar fotoiniciada de metacrilatos.

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FABRÍCIO AULO OGLIARI

USO DO HEXAFLUORFOSFATO DE DIFENILIODÔNIO NA POLIMERIZAÇÃO RADICALAR FOTOINICIADA DE METACRILATOS.

Tese apresentada ao Programa de Pós-Graduação em Odontologia, Área de Concentração Dentística da Faculdade de Odontologia de Pelotas da UNIVERSIDADE FEDERAL DE PELOTAS, como requisito parcial à obtenção do título de Doutor em Dentística.

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DEDICATÓRIA

Dedico este trabalho:

Aos meus familiares que estiveram sempre ao meu lado mesmo a quilômetros de distância e entenderam as minhas ausências nos almoços e churrascos de família durante esses anos de concentração extrema.

NOTA PRELIMINAR

A presente Tese foi redigida segundo o Manual de Normas para Dissertações, Teses e Trabalhos Científicos da Universidade Federal de Pelotas de 2006, adotando o Nível de Descrição 4 – Estruturas em Artigos, que consta no Apêndice D do referido manual.

RESUMO

OGLIARI, Fabrício Aulo. **Uso do hexafluorfosfato de difeniliodônio na polimerização radicalar fotoiniciada de metacrilatos.** 2009. 86f. Tese de Doutorado – Programa de Pós Graduação em Odontologia. Universidade Federal de Pelotas, Pelotas.

O objetivo do presente projeto foi avaliar o uso do hexafluorfosfato de difeniliodônio (DPIHFP) na polimerização radicalar de metacrilatos para aplicação odontológica. Para tal fim, foram considerados: aspectos relacionados ao potencial de sensibilização do DPIHFP pela canforoquinona; velocidade da reação de polimerização em sistemas binários e ternários; efeito em sistemas contendo solvente orgânico; e, influência nos valores e estabilidade da resistência de união ao tecido dentinário. Uma resina adesiva modelo constituída de 50% de Bis-GMA, 25% de TEGDMA e 25% de HEMA em massa foi formulada e utilizada em todos os experimentos realizados. Para a avaliação da cinética de conversão foram realizadas análises em espectroscopia no infravermelho em tempo real (RT-FTIR). Para a avaliação da resistência de união em dentina bovina, foram realizados ensaios de resistência de união à microtração na configuração de palitos, após 24 horas e 1 ano de realização das restaurações. Quando CQ foi utilizada como fotoiniciador, uma lenta reação de polimerização foi observada, sendo que a adição do DPIHFP como co-iniciador promoveu um aumento na reatividade do sistema, independentemente da concentração utilizada. A utilização de DPIHFP no sistema de fotoiniciação promoveu um aumento expressivo na reatividade do sistema, aumentando a taxa de polimerização máxima e o grau de conversão final do material. Adicionalmente, o DPIHFP reduziu o efeito inibitório provocado pela presença de solvente durante a polimerização, mantendo as taxas de polimerização semelhantes ao controle sem solvente. Quando o DPIHFP foi introduzido em um adesivo odontológico, foi observado um aumento significativo dos valores de resistência de união, sendo que estes valores mantiveram-se constantes em avaliação após 1 ano.

Palavras chave: polimerização; iodônio; grau de conversão.

ABSTRACT

OGLIARI, Fabrício Aulo*.* ***Diphenyliodonium hexafluorphosphate effect on the radical polymerization of methacrylates.*** *2009. 86f. Thesis* – Programa de Pós Graduação em Odontologia. Universidade Federal de Pelotas, Pelotas.

The present investigation evaluated the effect of the diphenyliodonium hexafluorphosphate (DPIHFP) on the radical polymerization of methacrylates. Rate of polymerization from binary and ternary photoinitiation systems, performance of such systems in the presence of solvent and its effects on the bonding strength to bovine dentin were investigated. As a model adhesive resin, a blend of Bis-GMA, TEGDMA and HEMA (50/25/25 %wt) was prepared. Real-time degree of conversion was performed in a Fourier transform infrared spectrometer. To assess the photoinitiator system efficiency in a dental adhesive composition, the adhesion between the model resin and bovine dentin was investigated using microtensile bond strength (µTBS). When CQ was used as photo-initiator, a slow polymerization reaction was observed. The addition of a second component (onium salt or amine) increases the polymerization rate and conversion independent on the co-initiator concentration. Ternary photo-initiator system showed an improvement on the polymerization rate of the dental adhesive model resin leading to high conversion in short photo-activation time. The addition of a solvent to the monomer blends decreased the polymerization kinetics, directly affecting the rate of polymerization, delaying vitrification, and attenuating the Trommsdorf effect. The introduction of DPIHFP displayed a strong increase in reaction kinetics, reducing the solvent inhibition effect. After one year of storage, the µTBS values of the group CQ+EDAB+DPIHFP showed significantly higher bond strength ($p<0.05$) than CQ, CQ+DPIHFP and CQ+EDAB groups and no difference from commercial adhesive group. The ternary photoinitiation system with DPIHFP maintained increased bond strength to dentin of model self-etching adhesive systems after one year of aging.

Keyowrds: *polymerization; iodonium; degree of conversion.*

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LISTA DE ABREVIATURAS

kcal/mol	quilocaloria por mol
UV	radiação ultravioleta
Nm	nanometro
℃	graus Celsius
h	hora
DPIHFP	*diphenyliodonium hexafluorphosphate* (hexafluorfosfato de difeniliodônio)
CQ	canforoquinona
EDAB	etil 4-dimetilamina benzoato
Bis-GMA	bisfenol A glicidil dimetacrilato
TEGDMA	trietilenoglicol dimetacrilato
HEMA	2-hidroxietil metacrilato
PMBOK	*Project Management Book of Knowledge* (sem tradução para o Português)
RT-FTIR	*real time Fourier transform infrared spectroscopy* (espectroscopia no infravermelho pela transformada de Fourier em tempo real)
ATR	*attenuated total reflectance* (reflectância total atenuada)
ZnSe	seleneto de zinco
°	graus
mm	milímetro
µl	microlitro
~	aproximadamente
cm^{-1}	por centímetro
mm/s	milímetro por segundo
IR	*infrared* (infravermelho)
SiC	carbeto de silício
cm	centímetro

ANOVA	*analysis of variance* (análise de variância)
mm^2	milímetro quadrado
PMMA	*poly(methyl methacrylate* (poli(metal metacrilato))
mm/min	milímetro por minuto
N	Newton
MPa	Megapascal
mol%	*weight percentage* (percentual em mol)
wt%	*weight percentage* (percentual em massa)
R_P	r*ate of polymerization (*taxa de polimerização)
R_P^{max}	*maximum rate of polymerization (*taxa máxima de polimerização)
s^{-1}	por segundo
t	tempo
Eq.	Equação
Fig.	Figura
O_2	gás oxigênio
s	segundo
CQ*	canforoquinona excitada
EtOH	etanol
µTBS	*Microtensile Bond Strength* (resistência de união à microtração)

SUMÁRIO

1 PROJETO DE PESQUISA

1.1 INTRODUÇÃO

Sais diariliodônio tendo um complexo haleto com um fraco contra-íon nucleofílico são eficientes fotoiniciadores para polimerizações catiônicas. A baixa energia da ligação C-I (entre 26 e 27 kcal/mol) permite, quando irradiado por luz, a decomposição do iodônio excitado em um radical cátion ariliodo, um radical arílico reativo e um ânion (CRIVELO e LAM, 1977). A grande maioria desses fotoiniciadores são sensibilizados quando irradiados na região do espectro com comprimento de onda abaixo dos 300nm, assim, fontes de luz ultravioleta (UV) são utilizadas. Apesar dessa técnica de fotoativação ser satisfatória para algumas aplicações como por exemplo tintas para impressões, na área biológica o uso de UV não é recomendado. Entretanto, é possível o uso como sensibilizadores, de corantes que absorvem na região do visível, que após a irradiação, reagem com os sais de iodônio, promovendo sua decomposição (LIN e STANSBURY, 2003). Dessa forma, é possível que sais de iodônio possam atuar na polimerização radicalar de metacrilatos (TIMPE et. al, 1993). Vários tipos de corantes sensibilizadores já foram investigados, como por exemplo a safranina (GOMEZ et. al, 2003), os derivados das acridinas (TIMPE et. al, 1993) e a acetofenona (LIN e STANSBURY, 2003).

Recentemente foi descrita na literatura uma via fácil de obtenção de sais orgânicos de iodônio (YOSHIDA et. al, 2007), possível através da reação do p-tolueno difluoreto com diversos organotrifluorboratos, em temperaturas brandas e obtendo rendimentos superiores à 80%, conforme Figura 1. Dessa forma espera-se que a exploração de sais de iodônio aumente significativamente em virtude da redução do seu custo de produção.

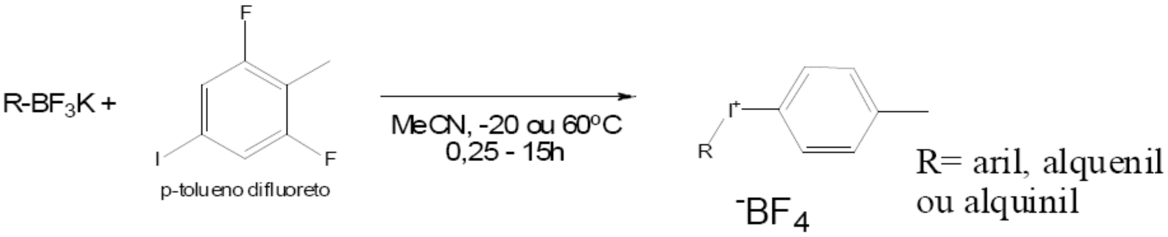
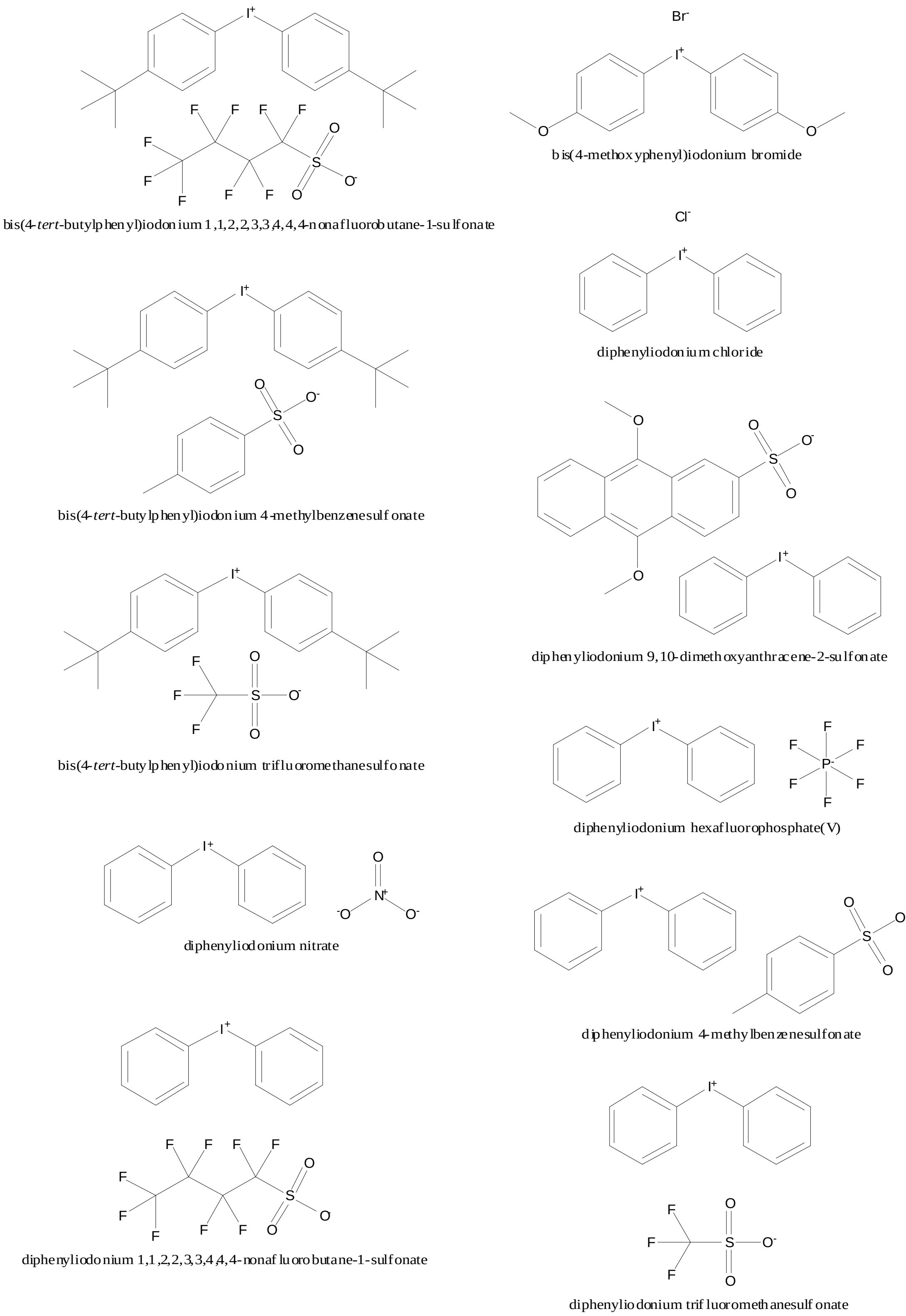


Figura 1. Reação em uma etapa para a obtenção de sais orgânicos de iodônio.

Utilizando a mesma rota sintética com derivados aromáticos, seria possível a obtenção de diversos outros tipos de sais de iodônio, como por exemplo, os ilustrados na Figura 2. Com esta vasta gama de possibilidades, aumentam as chances da obtenção de um composto que atenda às exigências básicas para o uso em materiais odontológicos, como por exemplo, estabilidade e biocompatibilidade.

No desenvolvimento de materiais odontológicos, principalmente em adesivos odontológicos, é possível descrever três importantes razões para o uso de um sal de iodônio na composição: seu caráter iônico permite sua hidrossolubilidade , o que é de grande interesse para a promoção da polimerização de monômeros polares em adesivos odontológicos, onde o fenômeno da separação de fase pode ocorrer (WANG et. al, 2006); a compatibilidade com compósitos a base de epóxidos (MILLICH et. al, 1998), como os recém introduzidos “siloranos”; e, o significativo aumento na taxa de polimerização (GOMEZ et. al, 2003), que é muito importante em sistemas que exigem uma rápida polimerização.



bis(4-*tert*-butylphenyl)iodonium 1,1,2,2,3,3,4,4,4-nonafluorobutane-1-sulfonate

bis(4-*tert*-butylphenyl)iodonium 4-methylbenzenesulfonate

bis(4-*tert*-butylphenyl)iodonium trifluoromethanesulfonate

diphenyliodonium nitrate

diphenyliodonium 1,1,2,2,3,3,4,4,4-nonafluorobutane-1-sulfonate

bis(4-methoxyphenyl)iodonium bromide

diphenyliodonium chloride

diphenyliodonium 9,10-dimethoxyanthracene-2-sulfonate

diphenyliodonium hexafluorophosphate(V)

diphenyliodonium 4-methylbenzenesulfonate

diphenyliodonium trifluoromethanesulfonate

Figura 2. Sais orgânicos de iodo com seus diferentes contra-íons (nomenclatura em inglês).

1.2 OBJETIVOS

O objetivo do presente projeto é a investigação da possibilidade de utilização de sais de iodônio em co-monômeros metacrilatos para aplicação odontológica. Para tal fim, as hipóteses abaixo relacionadas serão testadas:

- A canforoquinona, um corante amplamente utilizado como fotoiniciador para a polimerização radicalar de monômeros metacrilatos, pode atuar como um fotosensibilizador para o sal de hexafluorfosfato de difeniliodônio (DPIHFP);
- DPIHFP aumenta a reatividade do sistema fotoiniciador;
- DPIHFP como um co-iniciador, reduz o efeito inibitório de polimerização causado pela presença de solvente orgânico durante a fotopolimerização;
- DPIHFP aumenta os valores de resistência de união entre o adesivo e o tecido dentinário;
- DPIHFP aumenta a estabilidade da resistência de união entre o adesivo e o tecido dentinário após 1 ano de armazenagem;

1.3. MATERIAIS E MÉTODOS

1.3.1 Mecanismos gerenciais de execução

O gerenciamento da execução do projeto será feito pelo PMBOK (*Project Manager Book of Knowledge, Project Manager Institute*) com o auxílio da ferramenta MS Project (Microsoft) que atuarão junto aos objetivos propostos dentro de parâmetros de qualidade determinados, obedecendo a um planejamento prévio de prazos (cronograma) e custos (orçamento). Ou seja, dadas as metas e as restrições de recursos e tempo, caberá ao gerente do projeto garantir que ele atingirá os objetivos propostos. Dessa forma os mecanismos gerenciais serão divididos nas 9 áreas do conhecimento de gestão de projetos: Escopo, Tempo, Custo, Qualidade, Aquisições, Comunicação, Riscos, Pessoas e Integração.

1.3.2 Plano de Gerenciamento do Projeto

O plano de gerenciamento do projeto tomará como base a Estrutura Analítica do Projeto da Figura 3.

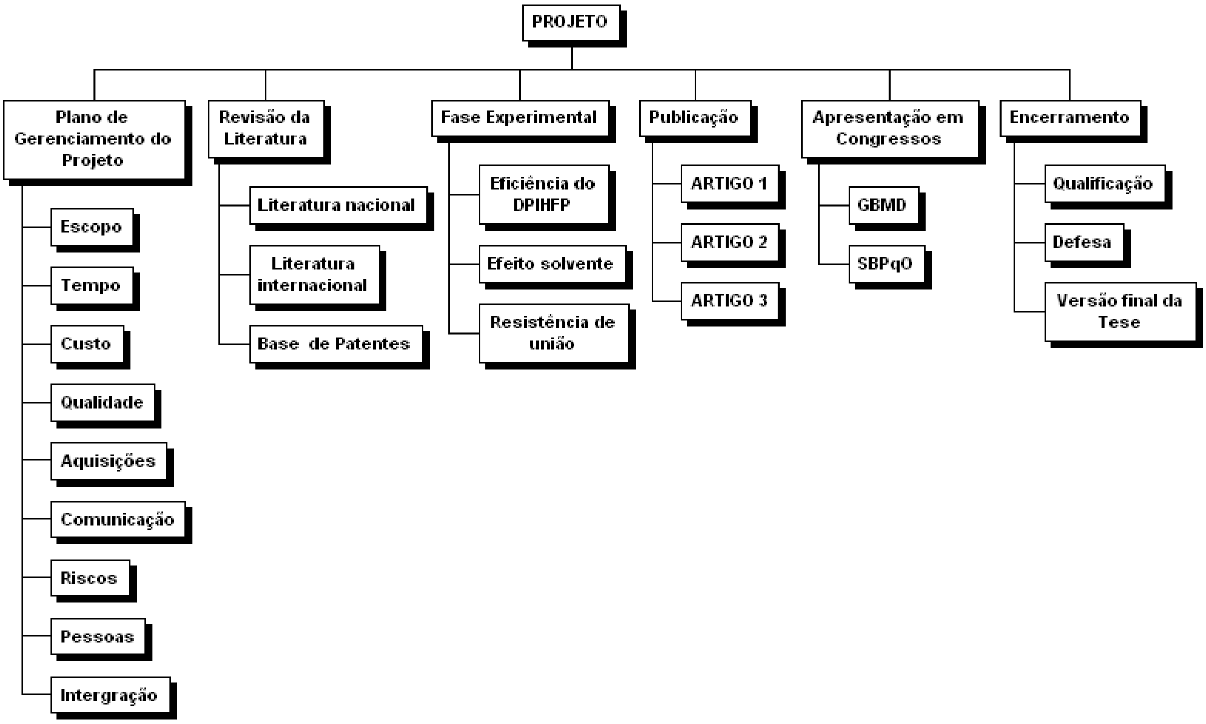


Figura 3. Estrutura Analítica do Projeto.

1.3.3 Reagentes

Bisfenol A glicidil dimetacrilato (Bis-GMA), trietilenoglicol dimetacrilato (TEGDMA), 2-hidroxietil metacrilato (HEMA) e canforoquinona (CQ), serão adquiridos junto ao fornecedor Esstech Inc (Essignton, EUA) e utilizados sem purificações adicionais. O etil 4-dimetilamina benzoato (EDAB) e o hexafluorfosfato de difeniliodônio (DPIHFP) serão adquiridos da Fluka (Milwaukee, EUA). Etanol absoluto será adquirido junto a empresa Synth (Synth, Brasil). Para a realização da fotoativação em todos os experimentos, será utilizada uma unidade de fotoativação de lâmpada halógena (XL

3000, 3M ESPE, EUA), com irradiância confirmada por meio de um potenciômetro (Ophir Optronics, EUA). As estruturas moleculares dos compostos utilizados podem ser visualizadas na Figura 4.

1.3.4 Formulações

Uma resina adesiva modelo será formulada e utilizada em todos os experimentos realizados. Será utilizada para a composição da mesma, 50% de Bis-GMA, 25% de TEGDMA e 25% de HEMA em massa.

1.3.4.1 Eficiência do DPIHFP

Para a avaliação da eficiência do DPIHFP como co-iniciador na polimerização radicalar da resina modelo, serão avaliadas as formulações do Quadro 1:

Quadro 1. Composição dos grupos experimentais.

Grupos Experimentais – concentrações % molar																
Componentes	**CQ**	**CQ+DPIHFP**					**CQ+EDAB**					**CQ+EDAB+DPIHFP**				
CQ	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1
DPIHFP		0,25	0,5	1	2	4						0,25	0,5	1	2	4
EDAB							0,25	0,5	1	2	4	2	2	2	2	2

1.3.4.2 Efeito solvente

Para a avaliação da eficiência do DPIHFP em reduzir o efeito inibitório da presença de solvente durante a fotopolimerização, serão avaliadas as formulações do Quadro 2:

Quadro 2. Composição dos grupos experimentais.

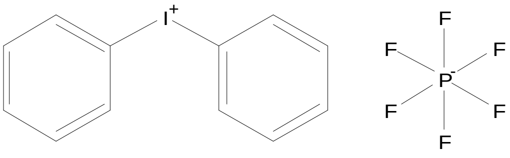
	Grupos Experimentais – concentração em massa									
Componentes	**CQ+EDAB***					**CQ+EDAB+DPIHFP ***				
Resina modelo + iniciadores	100	90	80	70	60	100	90	80	70	60
Etanol	0	10	20	30	40	0	10	20	30	40
Total:	**100**	**100**	**100**	**100**	**100**	**100**	**100**	**100**	**100**	**100**

1.3.4.3 Efeito na resistência de união

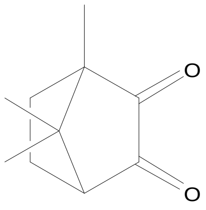
Para a avaliação do efeito do DPIHFP na resistência de união entre o adesivo e o tecido dentinário, serão avaliadas as formulações do Quadro 3:

Quadro 3. Composição dos grupos experimentais.

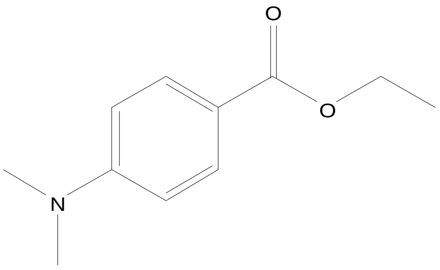
	Grupos			
Componentes	**A**	**B**	**C**	**D**
CQ	1	1	1	1
DPIHFP		1		1
EDAB			1	1
Resina modelo	99	98	98	97
Total:	**100**	**100**	**100**	**100**



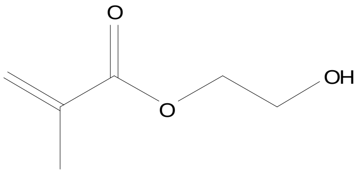
hexafluorfosfato de difeniliodônio



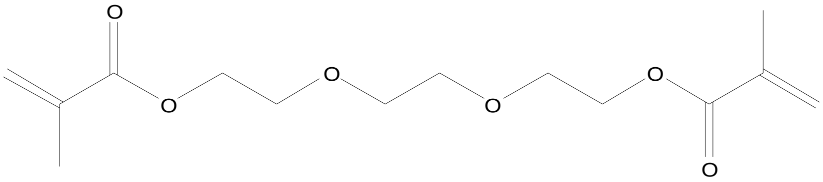
canforoquinona



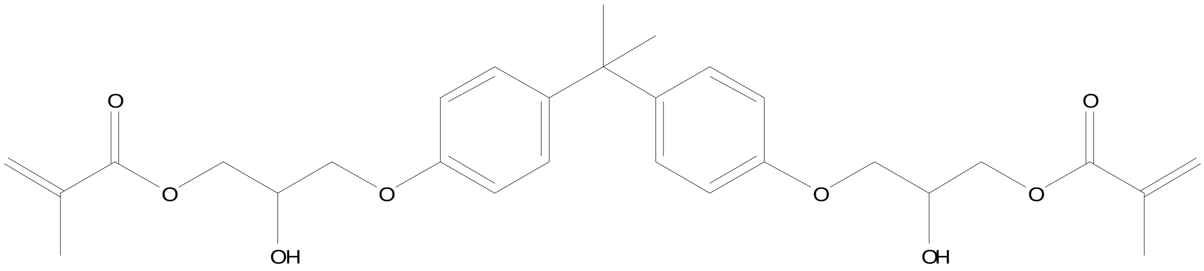
4-(dimethylamino)benzoato



2-hidroxietil metacrilato



trietilenoglicol dimetacrilato



bisfenol A glicidil dimetacrilato

Figura 4. Reagentes utilizados no estudo.

1.3.5 Ensaios laboratoriais

1.3.5.1 Cinética de Conversão

A cinética de conversão dos grupos será avaliada por meio de um espectrofotômetro infravermelho com Transformada de Fourier (RT-FTIR, Shimadzu Prestige21 Spectrometer, Shimadzu, Japão) equipado com dispositivo de reflectância total atenuada (ATR), composto por um cristal horizontal de seleneto de zinco (ZnSe), com espelhos de angulação de 45º (PIKE Technologies, EUA). Um suporte será acoplado para a fixação da unidade foto-ativadora ao espectrofotômetro, permitindo a padronização de uma distância de 5 mm entre a extremidade da ponteira de fibra ótica e a amostra (Figura 5). Cada amostra será dispensada diretamente no cristal de ZnSe (~3µl) e fotoativadas por até 60 segundos. Para o monitoramento de varredura será utilizado o software IRSolution, utilizando a apodização de Happ-Genzel, em uma faixa espectral entre 1750 e 1550 cm^{-1}, resolução de 8 cm^{-1} e velocidade de deslocamento de espelho de 2,8mm/s. A análise será realizada em ambiente com temperatura controlada de 23ºC e umidade relativa de <60%. O grau de conversão, por segundo, será calculado considerando a intensidade da vibração do tipo estiramento da dupla ligação carbono-carbono na freqüência de 1635 cm^{-1}. O estiramento simétrico do anel aromático em 1610 cm^{-1} das amostras polimerizadas e não polimerizadas será utilizado como padrão interno. Posteriormente, os dados obtidos serão plotados em uma curva ajustada pelo parâmetro regressivo não-linear de Hill 3.

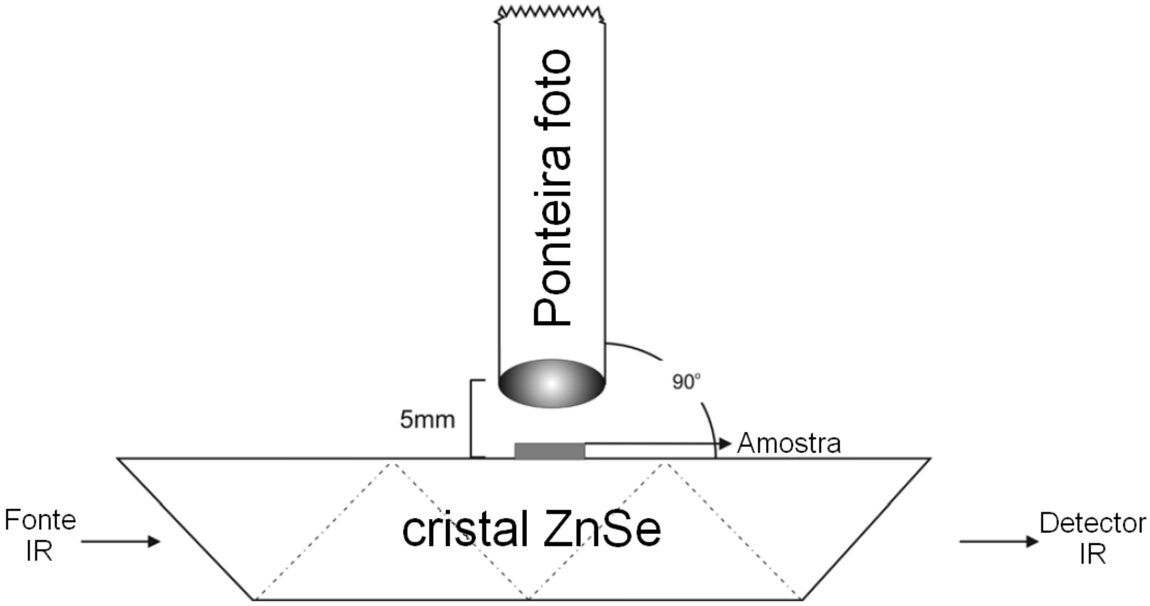


Figura 5. Configuração desenvolvida para a obtenção do grau de conversão em tempo real.

1.3.5.2 Resistência de união à microtração e análise do modo de fratura

Trinta incisivos bovinos, com período de extração inferior a três meses serão utilizados para esta avaliação. Após a extração e remoção da raiz e dos tecido periodontal e pulpar, os dentes serão armazenados em cloramina T 0,5% durante sete dias, sendo posteriormente transferidos para água destilada, transferidos para um freezer e mantidos congelados até seu uso. Na face vestibular dos dentes será realizado desgaste com lixas de SiC (carbeto de silício) de modo crescente até a exposição da dentina superficial. Em seguida a superfície será polida com lixa d’água granulação 600 sob abundante irrigação, no sentido de padronizar a espessura de lama dentinária formada. Os dentes serão lavados e a superfície de dentina será inspecionada em estereomicroscópio ótico com aumento 40X para assegurar a ausência de esmalte remanescente na superfície. Como ilustrado na Figura 6, um *primer* autocondicionante fosforado será aplicado vigorosamente sobre a dentina seca durante 30 segundos e em seguida será aplicado jato de ar a uma distância padronizada de 10 cm durante 10 segundos. O adesivo será aplicado e fotoativado por 20 segundos com aparelho fotopolimerizador XL 3000 (3M ESPE, EUA). A restauração será confeccionada utilizando quatro incrementos de 1 mm de compósito restaurador (C2 Charisma, Haerus Kulzer, Alemanha), sendo cada um destes fotoativados por 20 segundos.

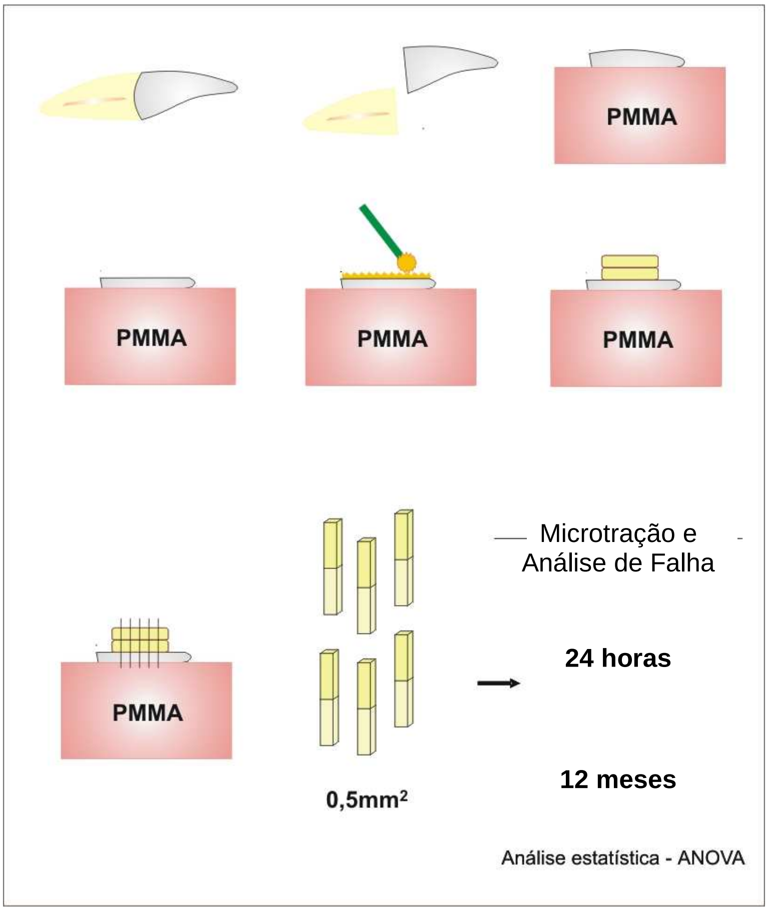


Figura 6. Representação esquemática do preparo das amostras para execução da metodologia de resistência de união à microtração que será utilizada.

Após armazenagem por 24 horas em água destilada à 37℃, os dentes serão seccionados em cortadeira de precisão (ISOMET 1000, Buheler). Serão realizados cortes de maneira a produzir palitos com área em sua secção transversa de aproximadamente 0,5mm^2, obtendo-se entre oito e doze palitos por dente, como ilustra a Figura 6. As amostras de cada grupo serão divididas em dois subgrupos à serem testados em diferentes períodos: após 24 horas e após 12 meses de armazenagem dos palitos em água destilada com 0,4% de azida sódica, à 37º (entre 15 e 20 palitos por grupo). Cada palito terá as dimensões mensuradas para cálculo da área de união utilizando um paquímetro digital com precisão de 0,01mm. Os palitos serão fixados em um dispositivo desenvolvido para ensaios de microtração com o auxílio de um adesivo à base de cianoacrilato (Super Bonder Gel, Loctite). As amostras serão tracionadas a uma velocidade de 0,5mm/min até sua falha em uma máquina de ensaio mecânico (Emic DL500) com uma célula de carga de 100N e a resistência de união mensurada (MPa).

Os dados obtidos serão submetidos à análise estatística. Todas as amostras fraturadas correspondentes à dentina serão observadas através de microscopia óptica (Futuretech FM 700, Japão) com um aumento de 100X e 500X para a determinação do modo de falha de cada amostra. As falhas serão classificadas em coesivas no adesivo, resina ou dentina, e adesiva. Acontecendo mais de um dos tipos de falha, esta será considerada uma falha do tipo mista.

1.3.5.3 Tratamento estatístico

O número de repetições especificados na presente metodologia partirão dos valores mais comumente utilizados na literatura. No entanto o número definitivo de repetições em cada avaliação terá como base o cálculo de amostra executado em estudos piloto prévios. De posse dos resultados dos experimentos, o método estatístico mais apropriado será escolhido com base na aderência no modelo de distribuição normal e igualdade de variâncias. Para todos os testes será considerado o valor $p<0,05$ como estatisticamente significante.

1.4 CRONOGRAMA

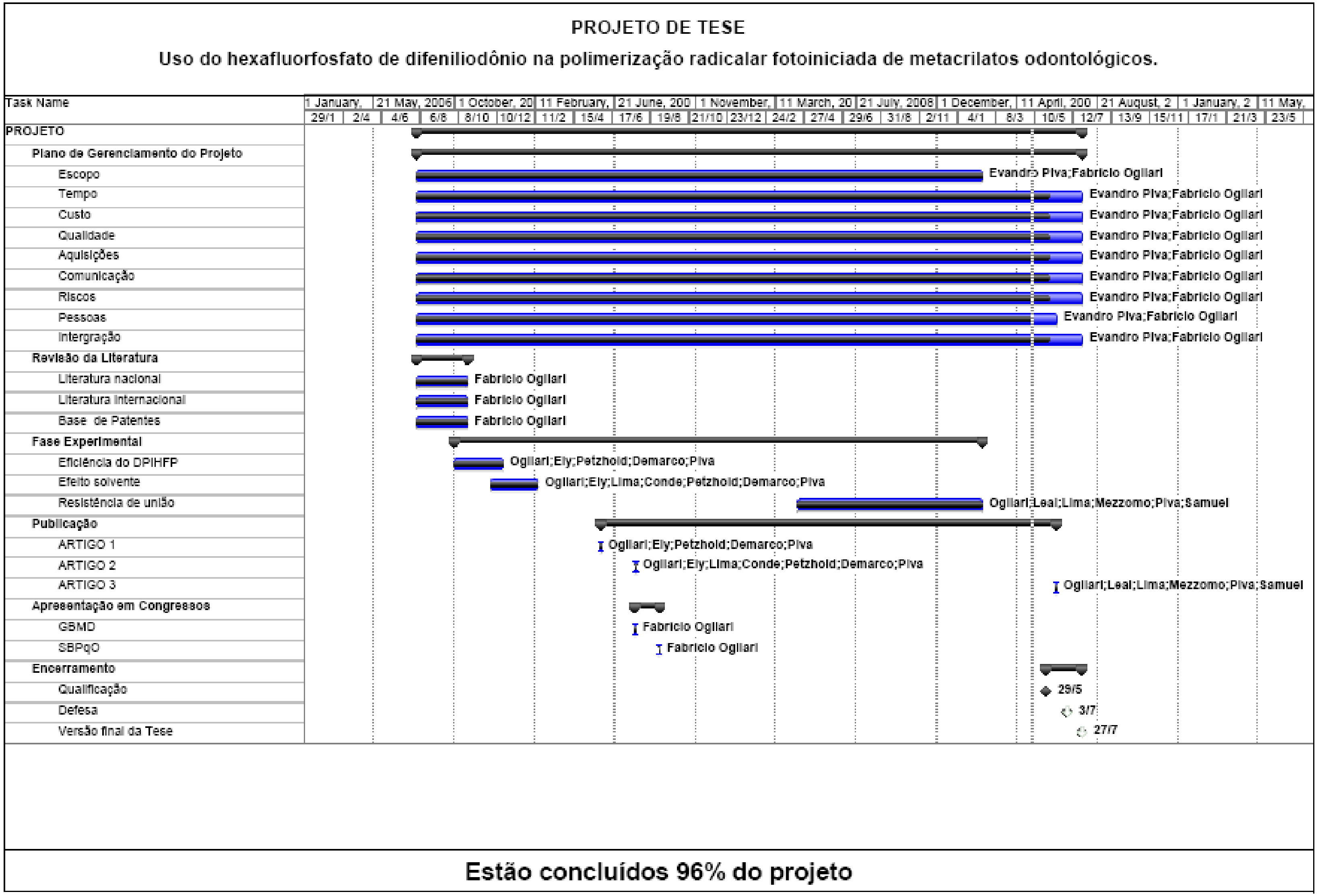


Figura 7. Gráfico de Gantt do projeto.

1.5 ORÇAMENTO

Quadro 4. Orçamento previsto para o projeto.

Itens	**Preço**
Reagentes	R$ 15.000,00
Material de Escritório	R$ 500,00
Materiais descartáveis	R$ 500,00
Vidraria de laboratório	R$ 500,00
Equipamento de segurança	R$ 300,00
Diárias e Passagens de Congressos	R$ 3.000,00
Despesas com gráfica	R$ 200,00
Equipamentos	R$ 60.000,00
Total:	**R$ 80.000,00**

1.6 FINANCIAMENTO

Este projeto conta com os seguintes financiamentos:

- R$15.000,00 adquiridos junto ao órgão de fomento FAPERGS através do edital PROADE 3 em 2006;
- apoio do fornecedor Esstech para o suprimento de monômeros e de canforoquinona;
- aporte de recursos financeiros da empresa Angelus Ciência e Tecnologia de aproximadamente R$ 10 mil para a execução do projeto;
- Edital FINEP CT-Infra 2006 com um aporte de R$ 60.000,00 para aquisição de um espectrofotômetro FTIR.

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2. ARTIGO 1 [*]

Título: Onium salt improves the polymerization kinetics in an experimental dental adhesive resin

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2.1 Abstract

The aim of this study was to evaluate the influence of an onium salt in the polymerization kinetics of a dental adhesive model resin. A monomer mixture, based on Bis-GMA, TEGDMA and HEMA, was used as a model dental adhesive resin, which was polymerized using camphorquinone (CQ) as a photo-initiator in addition to either binary or ternary photoinitiator systems. The binary systems were formulated with different concentrations of diphenyliodonium hexafluorphosphate or ethyl 4-dimethylaminobenzoate in relation to the monomer and 1 mol% of CQ. The ternary system was a blend of 1 mol% of CQ, 2 mol% of ethyl 4-dimethylamino benzoate and 0.25, 0.5, 1, 2 or 4 mol% of onium salt. Real time Fourier Transform infrared spectroscopy was used to investigate the polymerization reaction over the photo-activation time. When CQ was used as photo-initiator, a slow polymerization reaction was observed and a lower monomer conversion. The addition of a second component (onium salt or amine) increases the polymerization rate and conversion independent on the co-initiator concentration. Ternary photo-initiator system showed an improvement on the polymerization rate of the dental adhesive model resin leading to high conversion in short photo-activation time. Also, a mechanism for initiating polymerization using an amine or onium salt as a co-initiator component is proposed.

Keywords: Onium salt; Camphorquinone; EDAB; Dental adhesive; Real time infrared; Polymerization kinetics; Polymerization mechanism.

2.2 Introduction

Diaryliodonium salts, with a complex metal halide as a weakly nucleophilic counterion, are efficient photo-initiators for cationically mediated polymerization. The very low bond energy of the C–I bond (between 26 and 27 kcal/mol) allows, when light irradiated, the decomposition of the excited iodonium to an aryliodo radical-cation, a reactive aryl radical and an anion.[1] Most of these photo-initiators are active when irradiated in a light range below 300 nm, therefore, UV light sources are used. Although this activation strategy is satisfactory in some applications, such as paints and coatings, the use of UV light is not recommended in the biological field. However, it is possible that using dyes that absorb in the visible light region as sensitizers, would allow a reaction with the onium salts, promoting decomposition.[2] In this way, it is possible that onium salts can also act in the radical polymerization of methacrylates.[3] Several kinds of visible light sensitizer dyes have been investigated, such as safranine,[4] acridine derivatives[3] and acetophenone dyes.[2]

In the development of dental adhesives, there are three important reasons to use an onium salt: water-solubility, due its ionic character that can promote the polymerization of hydrophilic monomers in dental adhesives when phase separation occurs[5]; compatibility with epoxy-based resin composites[6]; the significant increase on the polymerization rate[4] which is very important in systems that need a fast cure.

It is hypothesized that camphorquinone, a dye widely used as a photo-initiator for radical polymerization in dental materials, can act as a photo-sensitizer to diphenyliodonium hexafluorphosphate, which does not absorb light in the visible region, improving the reactivity of the photo-initiator system.

The aim of this study is to evaluate the influence of an onium salt on the polymerization kinetics of an experimental dental adhesive model resin. Real time infrared spectroscopy was performed and the effect of the onium salt and tertiary amine concentration was investigated.

2.3 Method and Material

2.3.1 Reagents

Bisphenol A glicidyl dimethacrylate (Bis-GMA), triethylene glicol dimethacrylate (TEGDMA), 2-hydroxyethyl methacrylate (HEMA) and camphorquinone (CQ) were supplied by Esstech Inc. (Essignton, PA, USA) and used without further purification. Ethyl 4-dimethylaminobenzoate (EDAB) and diphenyliodonium hexafluorphosphate (DPIHFP) were purchased from Aldrich Chemical Co (Milwaukee, WI, USA) and used without further processing. To perform the monomer photo-activation, a halogen light-activation unit (XL 3000, 3 M ESPE, St. Paul, MN, USA) was used and the irradiation value (700 mW/cm^2) was confirmed with a digital power meter (Ophir Optronics, Danvers, MA, USA).

2.3.2 Formulations

A model dental adhesive resin was formulated through intensive mixing of 50 wt.% Bis-GMA, 25 wt.% TEGDMA and 25 wt.% HEMA. CQ was added at 1 mol% for all groups, according to the monomer moles. Four initiator systems were investigated at various levels: 1mol% of CQ; 1mol% of CQ and DPIHFP (0.25, 0.5, 1, 2 and 4mol%); 1mol% of CQ and EDAB (0.25, 0.5, 1, 2 and 4mol%); 1 mol% CQ + 2 mol% EDAB and DPIHFP at different molar concentrations. No radical scavenger was added to avoid interference on the polymerization kinetics.

2.3.3 Kinetics of polymerization by RT-FTIR spectroscopy

The degree of conversion from the experimental materials was evaluated using real time Fourier Transform infrared spectroscopy with a Shimadzu Prestige21 spectrometer, equipped with an attenuated total reflectance device. The reflectance devise was composed of a horizontal ZnSe crystal, with a 45° mirror angle (PIKE Technologies, Madison, WI, USA). A support was coupled to the spectrometer, fixing the light curing unit in place and standardizing the distance between the fiber tip and the sample at 5 mm. The IRSolution software (SHIMADZU, Columbia, MD, USA) was used in the monitoring scan mode, using the Happ-Genzel appodization, at a range of 1750 and 1550 cm^{-1}, resolution of 8 cm^{-1} and mirror speed of 2.8 mm/s. With this setup, one scan every 1 s during photoactivation was acquired. Analysis was performed at a controlled room temperature of 23℃ (±2℃) and 60% (±5%) relative humidity. The sample (3 µL) was directly dispensed on the ZnSe crystal and photo-activation was performed for 60 s. The degree of conversion was calculated as described in a previous study,[7] considering the intensity of carbon–carbon double bond stretching vibrations (peak height) at 1635 cm^{-1} and using the symmetric ring stretching at 1610 cm^{-1} from the polymerized and non-polymerized samples as an internal standard. Data were plotted and curve fitting performed by Hill three parameter non-linear regression. Using these data, the polymerization rate (R_P (s^{-1})) was calculated as the degree of conversion at time t subtracted of degree of conversion at time t-1. The coefficient of determination was greater than 0.98 for all curves.

2.4 Results

In Fig. 1, typical RT-FTIR spectra in the region of 1550–1750 cm^{-1} of a photo-initiated polymerization shows the disappearance of the aliphatic carbon–carbon double bond at 1650 cm^{-1} as a function of the photo-activation time. The influence of different initiator systems on the kinetics of the photo-polymerization is presented in Fig. 2. The effect of a coinitiator dramatically reduced the photo-activation time required to reach a higher conversion when compared with the system without a co-initiator (1 mol% of CQ). Fig. 3 shows the polymerization rate profiles from the dental adhesive model resin with different co-initiator systems. When only 1 mol% of CQ was used, the maximum rate of polymerization (R_P^{max} (s^{-1})) values were very low (in fact, undetectable), however, for the ternary photo-initiator system, the R_P^{max} was 66% higher than the CQ-EDAB system.

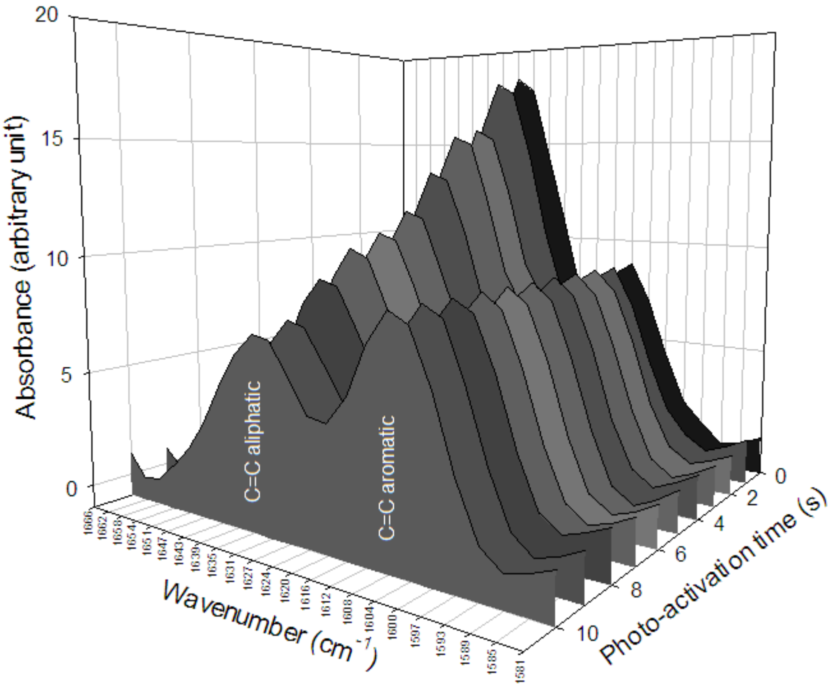


Figure 1: RT-FTIR spectra in the region (1550-1662 cm^{-1}) for a photopolymerization reaction as function of the photoativation time.

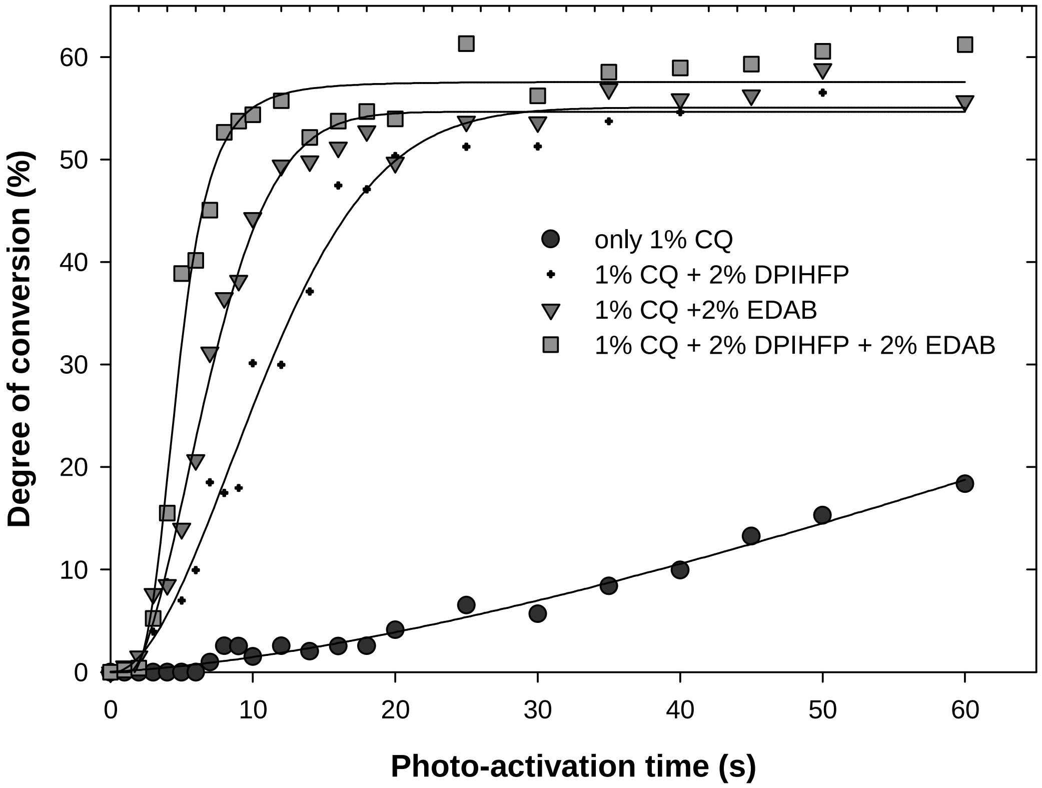


Figure 2. Degree of conversion for the photopolymerization of a dental model resin using different photo-initiatior systems.

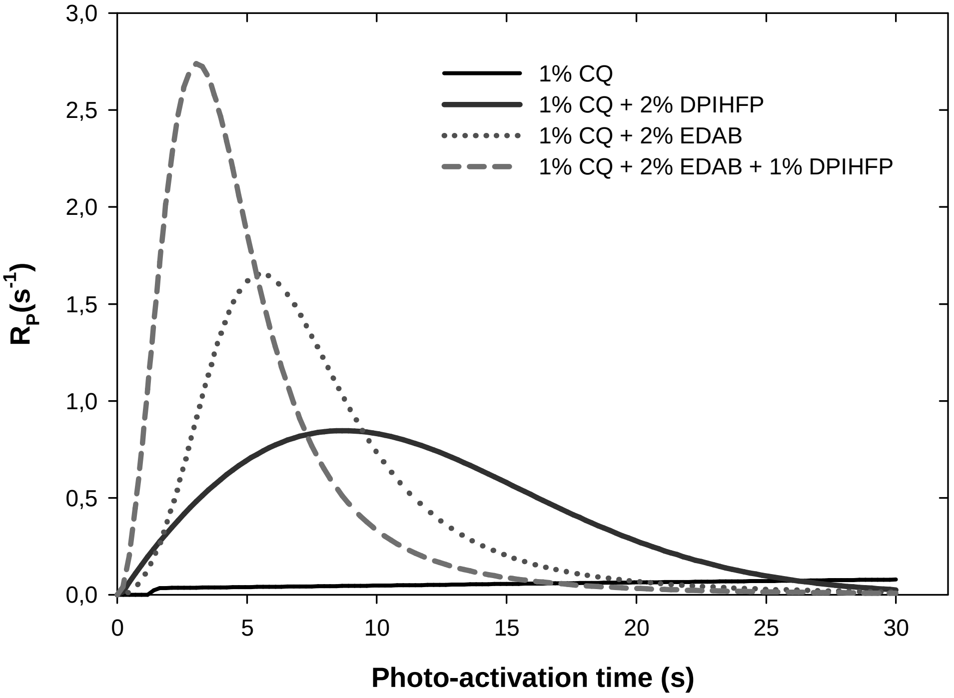


Figure 3. Rate of polymerization profiles of the resin using different photo-initiator systems.

When amine was used as a co-initiator, the R_P^{max} values were 1.33, 1.74, 1.57 and 1.65% per second for 0.25, 0.5, 1 and 2 mol% of EDAB, respectively. When 4 mol% of EDAB was used, a slight inhibitory effect was observed and the R_P^{max} decreased to 1.32% per second.

The influence of the DPIHFP concentration on the polymerization rate for the binary system is shown in Fig. 4. Higher R_P^{max} values were obtained with 2 and 4 mol%. The degree of conversion as a function of the photo-activation time, using a ternary initiator system, is shown in Fig. 5. As observed, independent on the DPIHFP mol%, similar monomer conversions were obtained after 10 s.

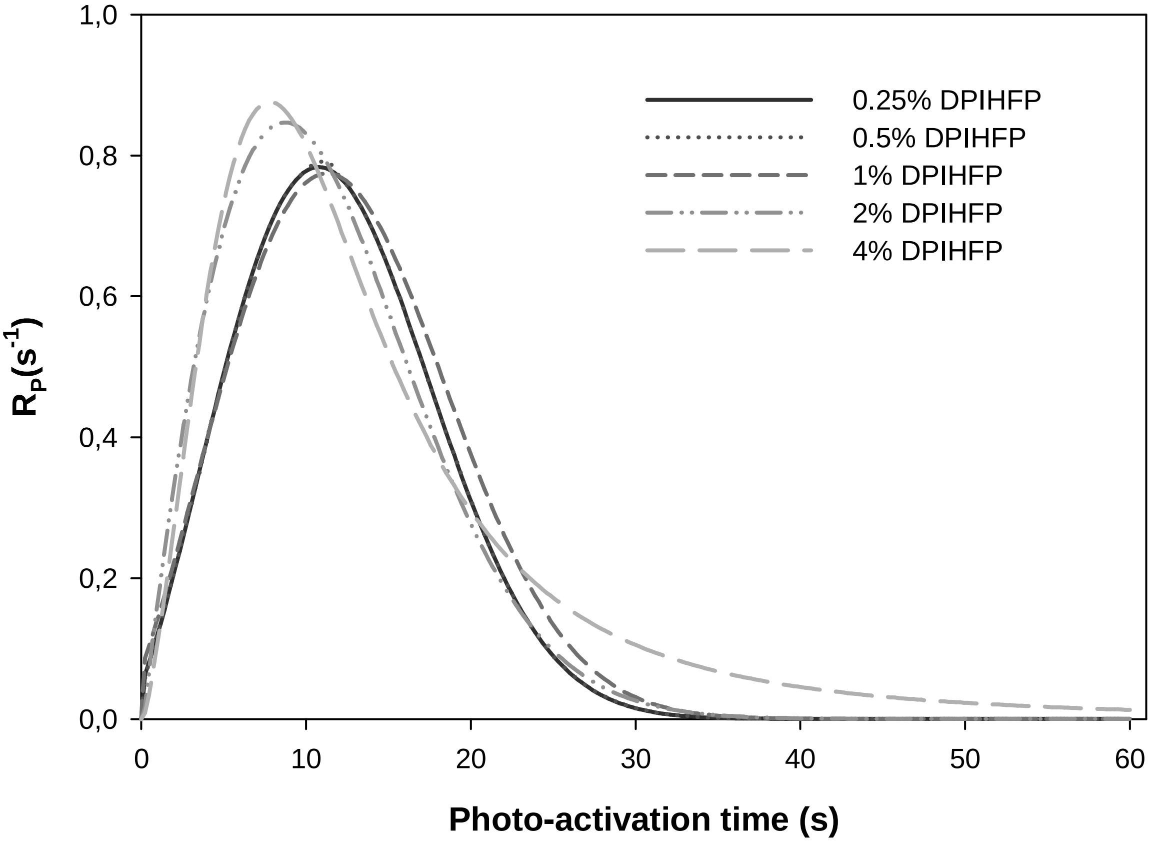


Figure 4. $R_P(s^{-1})$ as function of photo-activation time of the binary system at different DPIHFP concentrations (mol%).

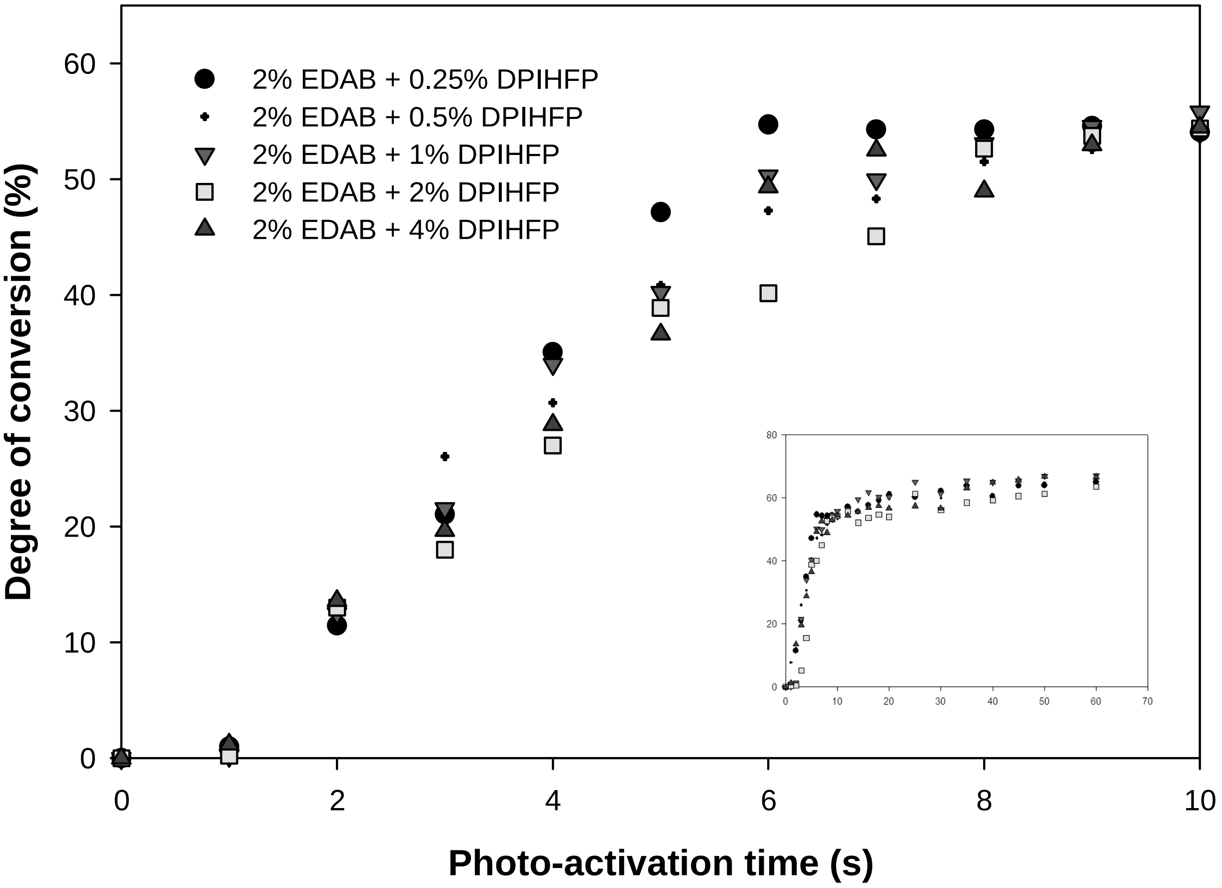


Figure 5. Degree of conversion over clinically convenient photo-activation time for ternary photo-initiator systems with different DPIHFP concentrations (mol%).

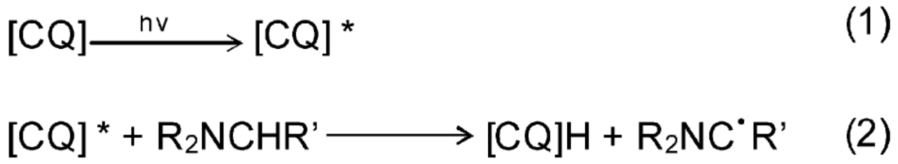
2.5 Discussion

Camphorquinone, an alpha dicarbonyl compound, a reactive excited species (CQ*) after light absorption, possesses a finite lifetime to react with the monomer and start the polymerization.[8] This explains the slow polymerization reaction when only camphorquinone was used as a photo-initiator (Figs. 2 and 3). After 60 s of photo-activation, only 18.3% of the monomer was consumed.

When EDAB was added into the monomer system, an increase of the polymerization rate at lower activation times was observed, even with lower concentrations. The beneficial role of the tertiary amines in photo-initiated free radical polymerization has been well recognized. Amines are very effective in reacting with the excited CQ* species (Eq. (1)), donating a proton (Eq. (2)) and generating free radicals, which can start the polymerization, as viewed in Scheme 1.[9]

Another mechanism that contributes to the efficiency of amine as a co-initiator is the free radical formation during the oxygen scavenging reaction (Scheme 2). Dissolved oxygen present in the monomer can react with the amine species, forming a peroxide radical (Eq. (3)) that can react with another

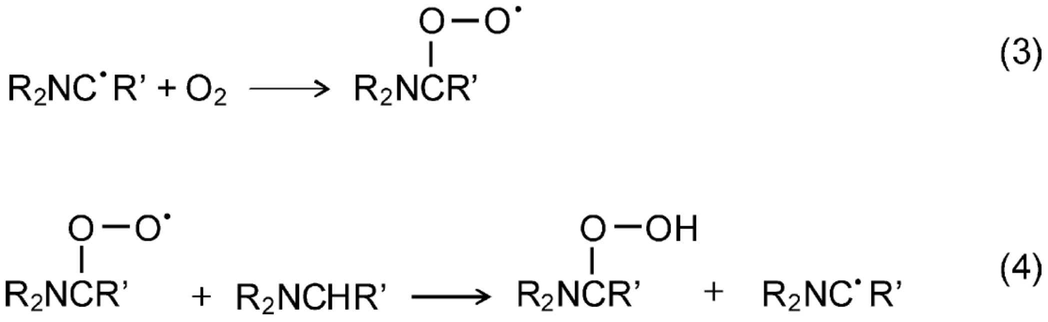
amine, releasing a new free radical (Eq. (4)).[2] In this way, the inhibitory effect of O_2 is attenuated.



$$[CQ] \xrightarrow{h\nu} [CQ]^{*} \qquad (1)$$

$$[CQ]^{*} + R_2NCHR' \longrightarrow [CQ]H + R_2NC^{\bullet}R' \qquad (2)$$

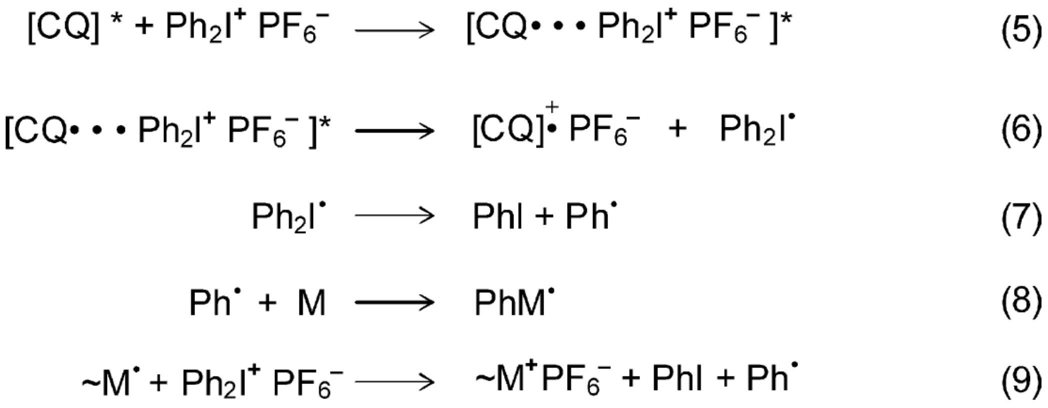
Scheme 1



$$R_2NC^{\bullet}R' + O_2 \longrightarrow R_2N\overset{\overset{O-O^{\bullet}}{|}}{C}R' \qquad (3)$$

$$R_2N\overset{\overset{O-O^{\bullet}}{|}}{C}R' + R_2NCHR' \longrightarrow R_2N\overset{\overset{O-OH}{|}}{C}R' + R_2NC^{\bullet}R' \qquad (4)$$

Scheme 2



$$[CQ]^{*} + Ph_2I^{+}PF_6^{-} \longrightarrow [CQ\bullet\bullet\bullet Ph_2I^{+}PF_6^{-}]^{*} \qquad (5)$$

$$[CQ\bullet\bullet\bullet Ph_2I^{+}PF_6^{-}]^{*} \longrightarrow [CQ]^{\overset{+}{\bullet}}PF_6^{-} + Ph_2I^{\bullet} \qquad (6)$$

$$Ph_2I^{\bullet} \longrightarrow PhI + Ph^{\bullet} \qquad (7)$$

$$Ph^{\bullet} + M \longrightarrow PhM^{\bullet} \qquad (8)$$

$$\sim M^{\bullet} + Ph_2I^{+}PF_6^{-} \longrightarrow \sim M^{+}PF_6^{-} + PhI + Ph^{\bullet} \qquad (9)$$

Scheme 3

The introduction of DPIHFP as co-initiator showed a significant effect on the monomer conversion, even at low mol%. Despite of the lower R_P^{max} values compared to the binary systems containing amine (Fig. 3), the deceleration stage was less abrupt and a similar degree of conversion after 20 s of photo-activation was reached (Fig. 2). DPIHFP concentration had little influence on R_P^{max}, indicating that even low concentrations of onium salt participate efficiently in the monomer polymerization. The mechanism that explains the role of an onium salt as a co-initiator when a dye is used (in the present study, CQ) as a photo-sensitizer is described elsewhere.[10] The electron-transfer photo-sensitization involves the absorption of light by CQ to give a corresponding excited species [CQ]*. As shown in Scheme 3, at blue light irradiation, an exciplex state is formed (Eq. (5)) and the onium salt is reduced by electron transfer (Eq. (6)). The diphenyliodine free radical formed is unstable and decomposes rapidly into phenyliodine and a phenyl free radical (Eq. (7)), making the reaction irreversible. These phenyl reactive species are effective in initiating the polymerization reaction (Eq. (8)). Radicals generated in the polymerization propagation are effective in cleaving the C–I bond, as viewed in Eq. (9), releasing another phenyl radical and allowing the polymerization reaction.

The ternary photo-initiator system, formed by CQ, EDAB and DPIHFP, showed an expressively higher R_P^{max} on the photoactivated polymerization. As presented in Fig. 3, the R_P^{max} for CQ/EDAB/DPIHFP systems reached 2.73% per second, while the binary system (CQ/EDAB), at the same reaction conditions, reached 1.65% per second. After 10 s of photo-activation using the ternary system, the monomer conversion was 54.4%, 44.3% for the binary system, and only 2.5% for CQ. This improvement of the monomer reactivity is of great value to the development of dental adhesives, reducing the required curing time. Most of the current commercially available dental adhesives request at least 10 s of photo-activation. As presented in Fig. 5, the DPIHFP concentration in a ternary system did not affect the degree of conversion after 10 s of photo-activation and just 0.25 mol% is enough to polymerize almost 60% of the monomers.

The reaction mechanism using a ternary photo-initiator system is more complicated to understand. In addition to the direct interaction of DPIHFP with the CQ triplet state, the amine radical generated from the exciplex state between CQ and EDAB (Eq. (2)) can react with DPIHFP, breaking the C–I bond and generating a reactive phenyl radical. The phenyl radicals (generated by CQ*-DPIHFP or through EDAB*-DPIHFP reactions) can further react with residual amines, abstracting a proton and generating a new amine free radical. This hypothesis is supported by a study[4] that observed an increase of the radical yield when diphenyliodonium chloride was used in a dye/amine/onium system to polymerize acrylamide. Since the DPIHFP concentration has no influence on the polymerization rate, and considering that it is totally soluble in the reaction medium, it can act as a catalyst by decreasing the activation energy of the photoinitiation. It is suggested by the current researchers that an exciplex between CQ* and DPIFHP is initially formed, which reacts further with the amine (EDAB), giving a radical amine species that intiates the polymerization and regenerates the DPIFHP, forming a new exciplex with a new photo-activated CQ (Scheme 4, Eq. (10)).

Although most of the adhesive systems presented an acceptable performance,[7] the long-term durability of dentin/resin interfaces is a concern.[11] Dentin adhesives are used in an environment that is adverse to acrylic polymerization, i.e. in presence of water and residual organic solvents.[12] Polymerization reaction kinetics when residual solvents are present are strongly reduced when considering a clinically convenient photo-activation time, which could be partially resolved with a more reactive polymerization system. Considering that the degree of conversion is directly related with polymer cross-linking,[13] a higher degree of conversion is required for a more durable polymer. Therefore, in addition to the advantage of DPIHFP on the polymerization kinetics, potentially reducing the material technique-sensitivity, the excellent water solubility enables this moiety to act when acrylic monomers, like the 2- hydroxyethyl methacrylate, are in aqueous solution. This is of particular importance because the degree of conversion for the resin also affects the biocompatibility of the adhesive system. Uncured methacrylate-based materials have negative effects when applied in human pulp,[14] resulting in cytotoxicity on culture cells, even at low concentrations.[15]

$$[CQ\bullet\bullet\bullet Ph_2I^+ PF_6^-]^* + R_2NCHR' \longrightarrow [CQ]H + R_2NC^{\bullet}R' + Ph_2I^+ PF_6^- \qquad (10)$$

Scheme 4

2.6 Acknowledgement

Authors were grateful to CAPES for the scholarship and to Esstech Inc. for reagents donation.

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3. ARTIGO 2 [*]

Título: Onium Salt Reduces the Inhibitory Polymerization Effect From an Organic Solvent in a Model Dental Adhesive Resin

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[*] **Artigo formatado segundo normas do periódico** Journal of Biomedical Materials Research Part B: Applied Biomaterials. **Publicado em 2008 como:** Onium Salt Reduces the Inhibitory Polymerization Effect From an Organic Solvent in a Model Dental Adhesive Resin. Journal of Biomedical Materials Research Part B: Applied Biomaterials. **86(1):113-118.**

3.1 ABSTRACT

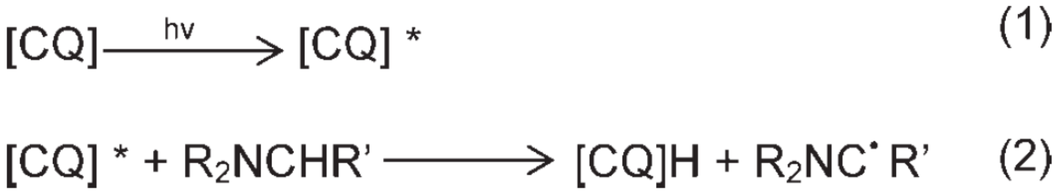
This study evaluated the effect of organic solvent concentration on the polymerization kinetics for a model dental adhesive resin containing a ternary photoinitiator system. A monomer blend based on the Bis-GMA, TEGDMA, and HEMA was used as a modeldental adhesive resin, which was polymerized using a binary system [camphorquinone (CQ) and ethyl 4-dimethylamine benzoate (EDAB)] and a ternary system [CQ, EDAB, and diphenyliodonium hexafluorphosphate (DPIHFP)]. Additionally, these blends had 0, 10, 20, 30, and 40 wt % ethanol added. Real-time Fourier transform infrared spectroscopy was used to investigate the polymerization reaction over photoactivation time. Data were plotted, and Hill's three-parameter nonlinear regression was performed for curve fitting. The addition of a solvent to the monomer blends decreased the polymerization kinetics, directly affecting the rate of polymerization, delaying vitrification, and attenuating the Trommsdorf effect. The introduction of DPIHFP displayed a strong increase in reaction kinetics, reducing the solvent inhibition effect. After 10 s of photoactivation, the binary system obtained in 0, 10, 20, 30, and 40% of ethanol, a degree of conversion of 44.6, 26.3, 13.4, 1.15, and 0.0%, respectively, whereas when a ternary system was used, the values were 54.6, 40.5, 27.4, 14.5, and 3.4%. An improvement was observed in the polymerization kinetics of a model dental adhesive resin when using a ternary photoinitiation system, making the material less sensitive to the residual presence of a solvent before photoactivation.

Keywords: onium salt; camphorquinone; EDAB; dental adhesive; real time infrared; solvent; polymerization kinetics; polymerization mechanism

3.2 INTRODUCTION

Dentin adhesives are composed of methacrylate-based monomers that undergo free-radical polymerization and provide adhesion of synthetic materials to dental tissues. To enhance the polarity of the comonomer blends and to reduce the resin viscosity, organic protic and aprotic solvents, such as ethanol and acetone, respectively, are introduced into these materials. This approach permits the infiltration of unpolymerized resin into wet partially demineralized dentin and allows the creation of an interdiffusion zone constituted by resin and collagen fibrils.[1]

Although the presence of a solvent is fundamental in obtaining a more homogeneous hybrid layer, volatization is required before monomer photoactivation can occur. The presence of residual solvent during polymerization reduces the polymer degree of conversion,[2] potentially creating a more porous dentin/adhesive interface.[3] These events are a challenge for the long-term performance of the adhesive. In a clinical context, the time required to complete the adhesive procedure is an aspect that has been considered by the clinicians. It is known that, even after 120 s of air drying, a considerable amount of residual solvent remains.[4] Thus, attention should be given to the technical variables, because the adhesive procedure is associated with the susceptibility of comonomer polymerization kinetics with regard to the residual solvent. Thus, theoretically, a way to improve the bonding performance is the development of a more effective photoinitiator system for dentin adhesives. Usually, to the polymerization of dental adhesives, a binary photoactivator system comprising camphorquinone (CQ) and amine is used (Scheme 1). Diaryliodonium salts, with complex metal halides as weakly nucleophilic counterions, are efficient photoinitiators for UV-irradiated monomer systems, which are extensively used in paints and coats.[5] In addition to UV light, it is possible that dyes that absorb in the visible light region can be used as sensitizers. After light irradiation, these dyes may react with the onium salts, promoting decomposition of free radicals suitable for the polymerization process.[6] With the use of ternary photoinitiator systems, including dye (like CQ), tertiary amine, and onium salts, it is expected that the polymerization reaction kinetics improve.[7] Another advantage for the use of onium salts as coinitiators in dental adhesives is its ionic character, enabling them to be water miscible.



Scheme 1.

The aim of this study is to evaluate the influence of an onium salt on the polymerization kinetics of a model dental adhesive resin containing different amounts of a protic organic solvent during polymerization.

3.3 MATERIALS AND METHODS

3.3.1 Reagents

Absolute ethanol (99.5%) was purchased from Nuclear (Nuclear, SP, Brazil). Ethyl 4-dimethylamine benzoate (98%, EDAB) and diphenyliodonium hexafluorphosphate (>98%, DPIHFP) were purchased from Aldrich Chemical (Milwaukee, WI) and were not modified before use. Bisphenol A glicidyl dimethacrylate (96%, Bis-GMA), triethyleneglicol dimethacrylate (96.5%, TEGDMA), 2- hydroxyethyl methacrylate (99.5%, HEMA) and camphorquinone (97%, CQ) were supplied by Esstech (Essignton, PA) and used without further purification. To perform the monomer photoactivation, a halogen light-activation unit (XL 3000, 3M ESPE, St. Paul, MN) was used, and the irradiance value was confirmed with a digital power meter (Ophir Optronics, Danvers, MA) to be 700 mW/cm^2.

3.3.2 Formulations

A dental adhesive model resin was prepared through the intensive mixture of 50 wt % of Bis-GMA, 25 wt % TEGDMA, and 25 wt % HEMA. Two photoinitiator systems were evaluated: a binary system (1 mol % of CQ and 1 mol % of EDAB) and a ternary system (1 mol % of CQ, 1 mol % of EDAB and 1 mol % of DPIHFP). For each photoinitiator system, different concentrations of absolute ethanol were added: 0, 10, 20, 30, and 40 wt %. No radical scavenger was added to avoid interference with the polymerization kinetics.

3.3.3 Kinetics of Polymerization by RT-FTIR Spectroscopy

The degree of conversion from the experimental materials were evaluated using real time Fourier Transform infrared spectroscopy with a Shimadzu Prestige21 spectrometer equipped with an attenuated total reflectance device composed of a horizontal ZnSe crystal, with a 45° mirror angle (PIKE Technologies, Madison, WI). A support was coupled to the spectrometer, fixing the light curing unit and standardizing the distance between the fiber tip the sample at 5 mm (Figure 1).

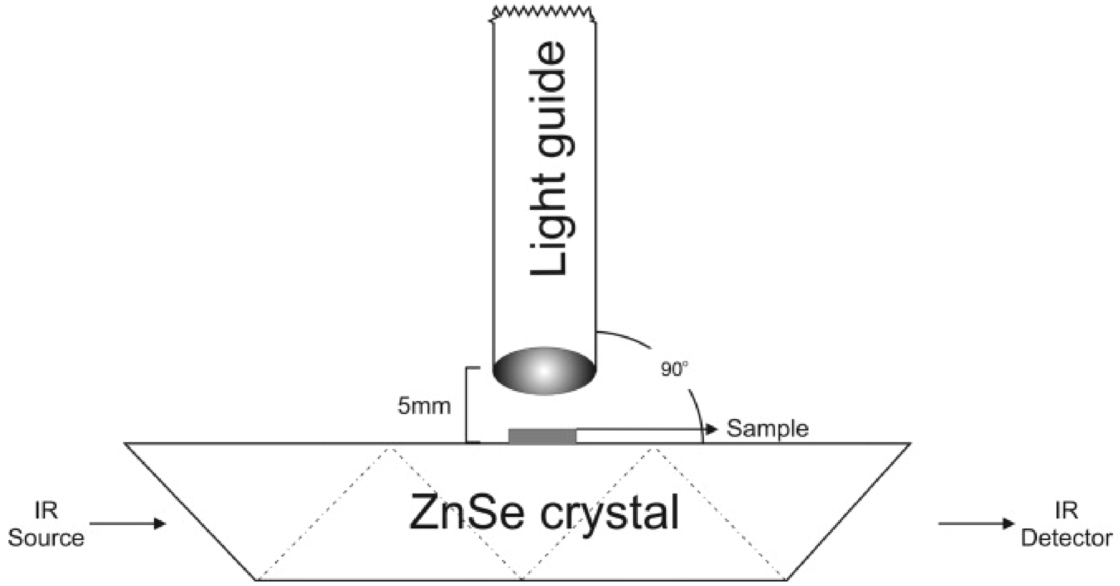


Figure 1. Schematic representation of the polymerization kinetics evaluation using RT-FTIR.

The monitoring scan mode of the IRSolution software (Shimadzu, Columbia, MD) was used, using the Happ-Genzel apodization, at a range of 1750 and 1550 cm^{-1}, resolution of 8 cm^{-1} and mirror speed of 2.8 mm/s. Using this setup, 1 scan every 1 second during photoactivation was acquired. Analysis was performed at a controlled room temperature of 23℃ and relative humidity <60%. The sample (3 µL) was directly dispensed by the ZnSe crystal and immediately the photoactivation and sample scanning was performed for 60 s. The degree of conversion was calculated as described in a previous study,[8] considering the intensity of carbon–carbon double-bond stretching vibration (peak height) at 1635 cm^{-1} and using, as an internal standard, the symmetric ring stretching at 1610 cm^{-1} from the polymerized and unpolymerized samples. The ethanol molecule does not absorb at the spectra range evaluated, thus, the solvent evaporation during the polymerization reaction did not affect the aliphatic and aromatic carbon–carbon double-bond measurements. Data were plotted, and Hill's three-parameter nonlinear regression was performed for curve fitting. The coefficient of determination was greater than 0.99 for all curves. The rate of polymerization (R_P^{max}) was calculated considering data fitting.

3.4 RESULTS

Figure 2 represents the effect of ethanol concentration on the polymerization kinetics from the model dental adhesive resins using CQ as a photoinitiator and EDAB as a coinitiator (binary system). An inhibitory polymerization effect was observed when a solvent was introduced to the monomer system. Considering 10 s as the common time intended for photoactivation of most adhesives, the degree of conversion obtained at this time for 0, 10, 20, 30, and 40% ethanol were 44.6, 26.3, 13.4, 1.15, and 0.0%, respectively.

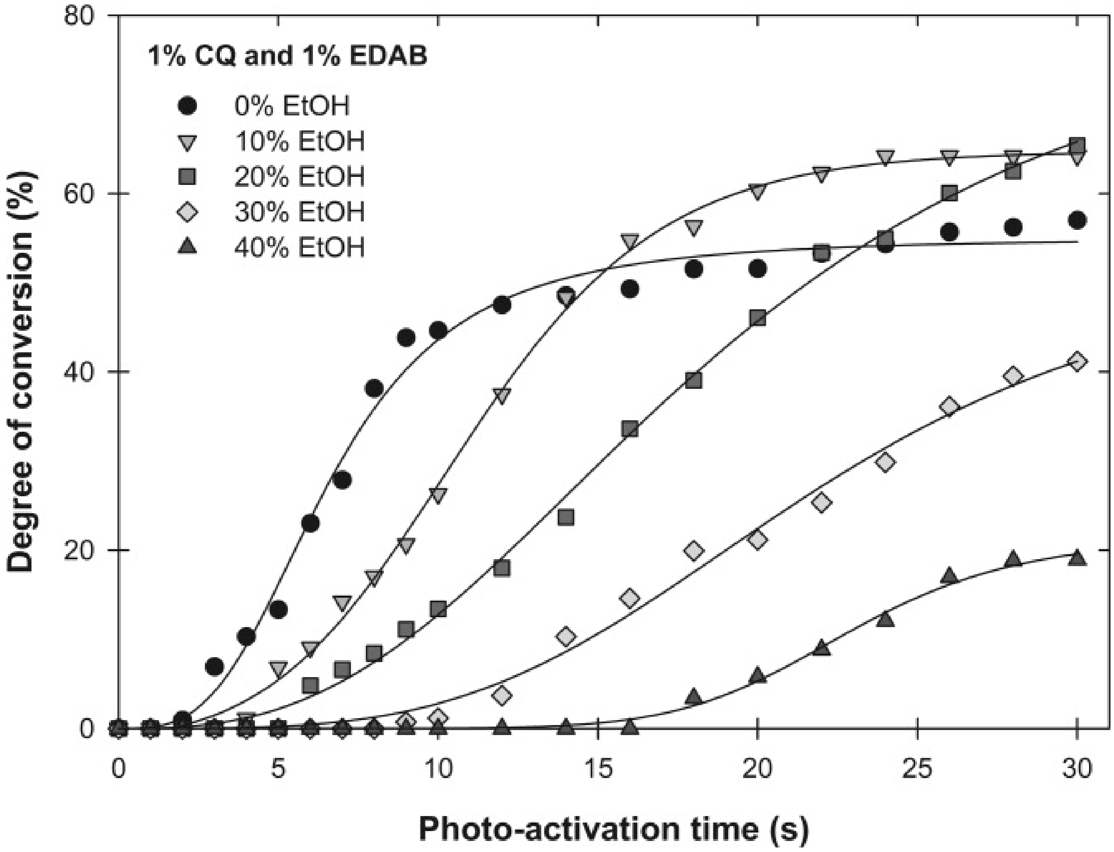


Figure 2. Polymerization kinetics from binary photoinitiator system with different amounts of ethanol. Legends: CQ, camphorquinone; EDAB, ethyl 4-dimethylamine benzoate; EtOH, ethanol.

The introduction of DPIHFP (ternary system) did not remove the inhibitory effect as observed in Figure 3, but the degree of conversion values found were higher than those of the binary system. With 10 s of photoactivation,

the degree of conversion from ternary systems containing 0, 10, 20, 30, and 40% of ethanol were 54.6, 40.5, 27.4, 14.5, and 3.4% respectively. A paired comparison is provided in Figure 4, in which the effect of DPIHFP was evident

for all groups.

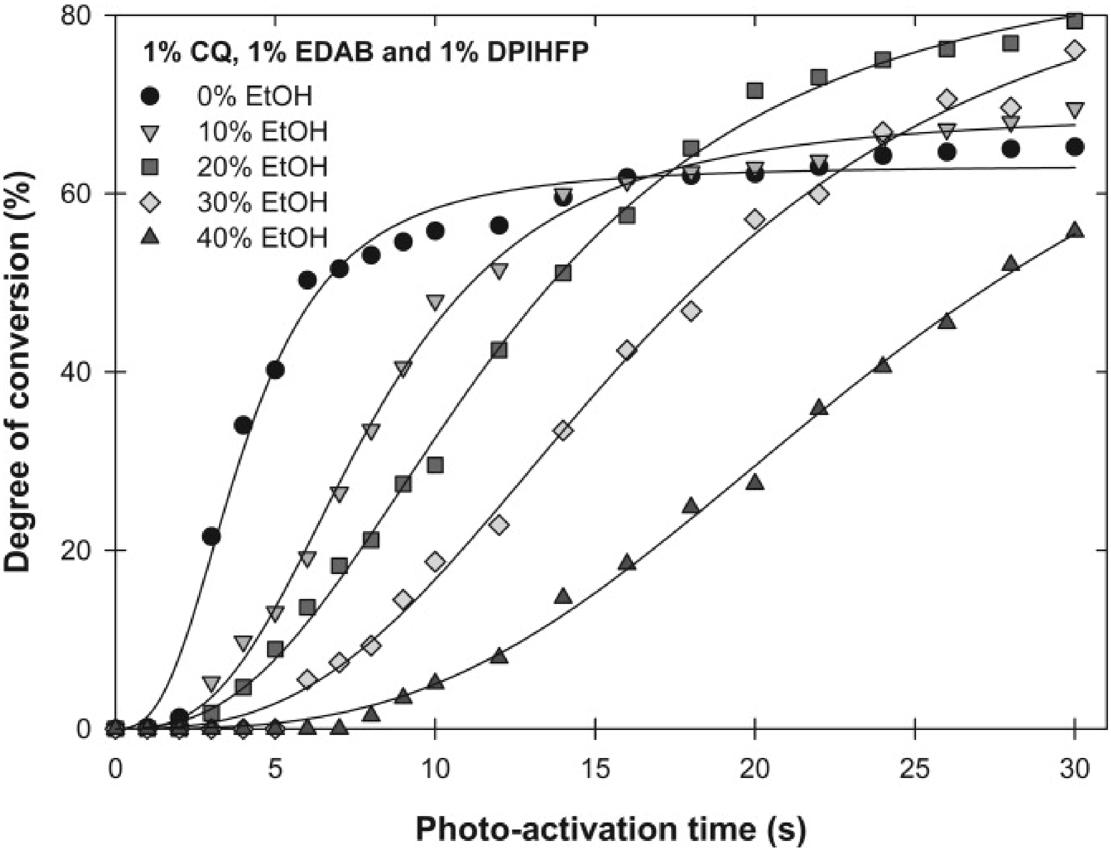


Figure 3. Polymerization kinetics from ternary photoinitiator system with different amounts of ethanol. Legends: CQ, camphorquinone; EDAB, ethyl 4-dimethylamine benzoate; DPIHFP, diphenyliodonium hexafluorphosphate; EtOH, ethanol.

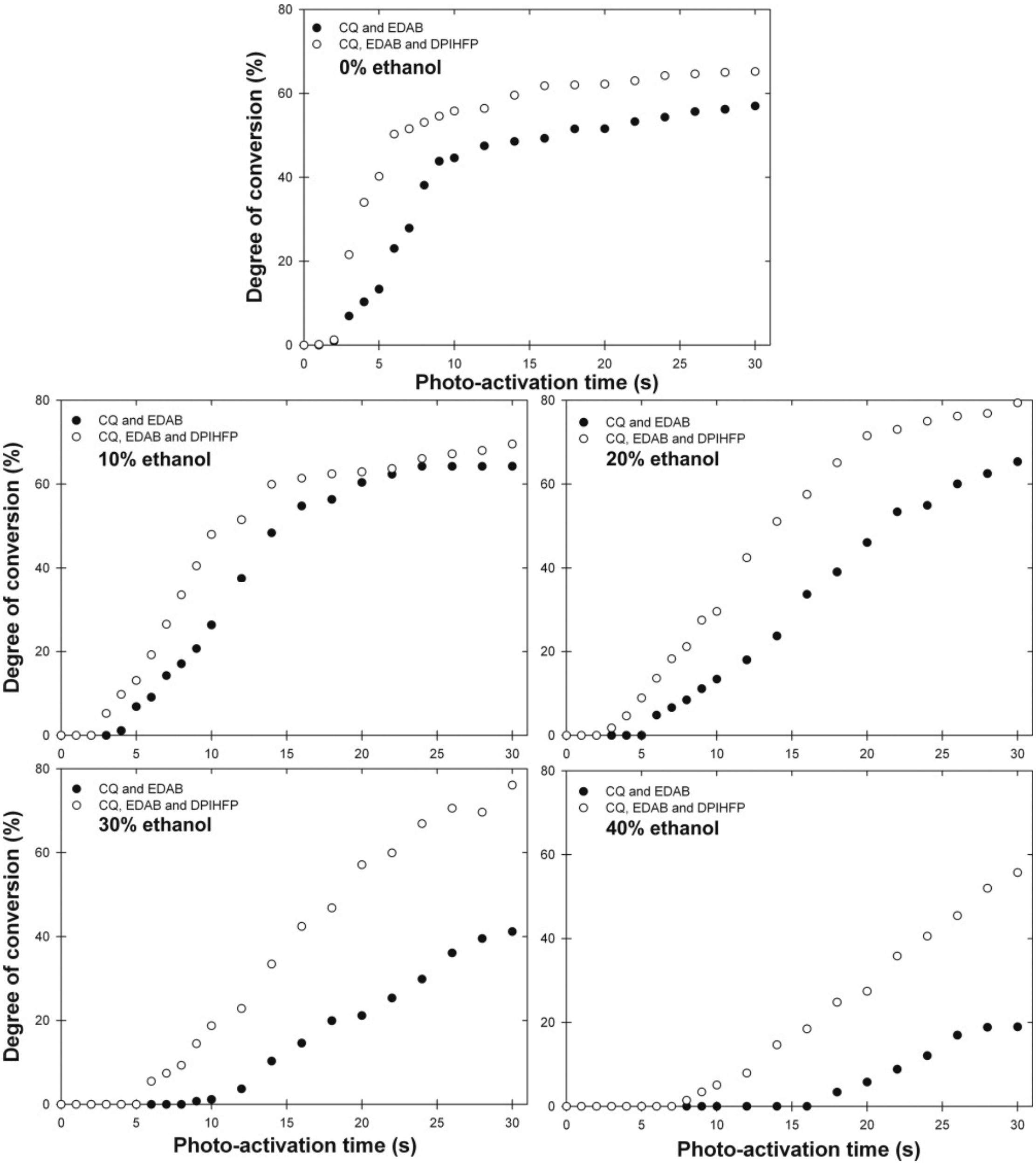


Figure 4. Effect of the DPIHFP on the degree of conversion over photoactivation time in each ethanol concentration. Legends: CQ, camphorquinone; EDAB, ethyl 4-dimethylamine benzoate; DPIHFP, diphenyliodonium hexafluorphosphate.

In Figure 5, the effect of DPIHFP on the rate of polymerization at different ethanol concentrations is shown. The R_P^{max}, independent of the ethanol amount, was higher in the ternary system. Also, it was observed that the curve inflection point was obtained at an earlier time.

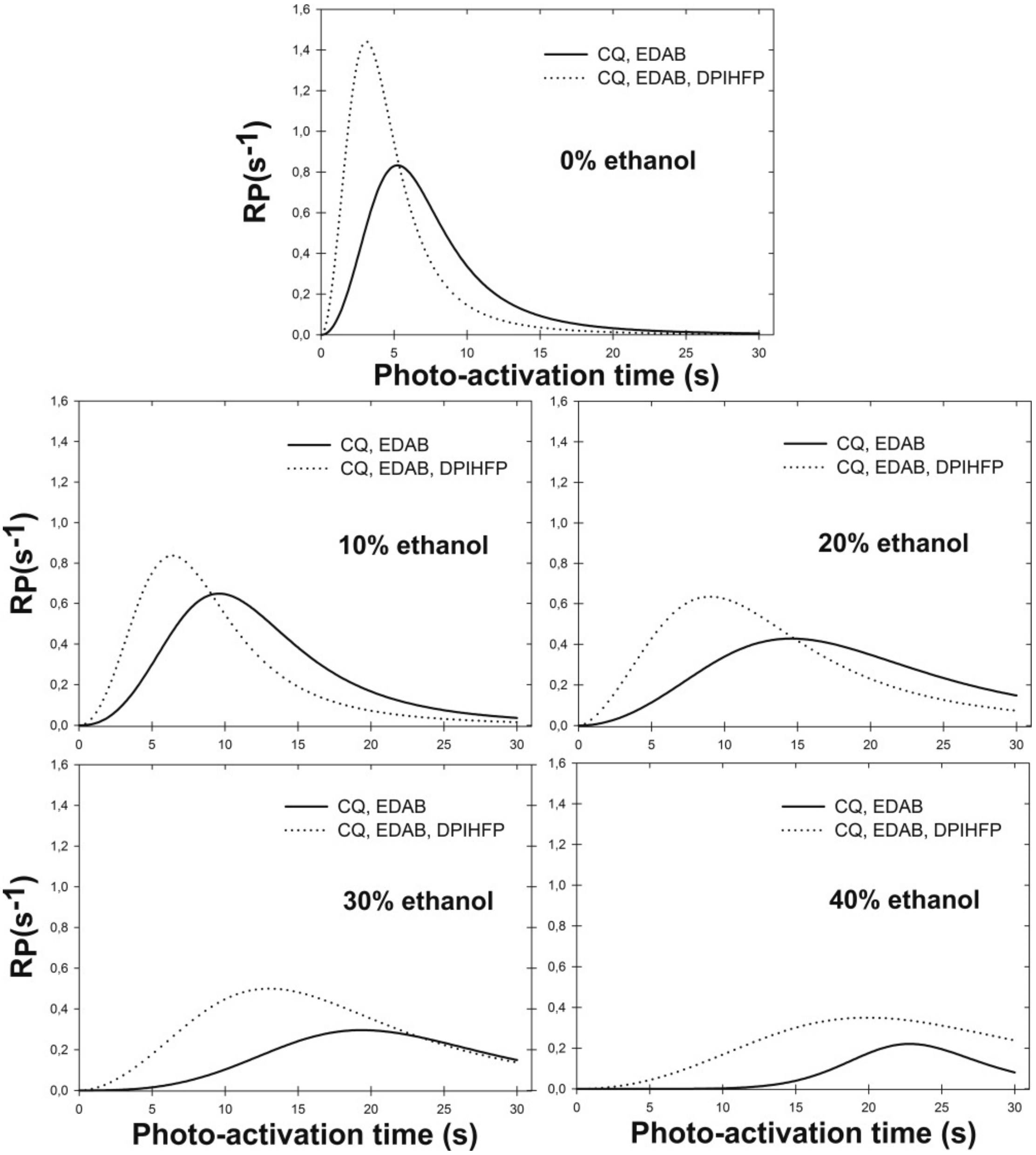


Figure 5. Comparison between the rate of polymerization from binary and ternary photoinitiator systems polymerized in different ethanol amounts. Legends: CQ, camphorquinone; EDAB, ethyl 4-dimethylamine benzoate; DPIHFP, diphenyliodonium hexafluorphosphate.

3.5 DISCUSSION

To polymerize dental methacrylate monomers with light exposure, CQ is widely used as a photoinitiator. CQ is an α-dicarbonyl compound that becomes a reactive species after light absorption and photolysis. CQ is classified as a type II photoinitiator, because it is necessary to use a second component for effective radical generation.[9] When used alone, the reactive species from CQ have a short lifetime, being ineffective to initiate the radical polymerization.[10] As a second component, or coinitiator, tertiary amines are used because of their efficiency as H-donor reagents.[9] These systems that use CQ and tertiary amines are called binary photoinitiator systems and are the most frequently used of the currently available dental adhesives. The reaction mechanism of CQ/amine combinations is shown in Scheme 1.

As viewed in Figure 2, the binary system was capable of promoting the monomer photopolymerization, reaching 57.0% conversion in the 0% ethanol group. In the group with 0% ethanol, the start of the carbon–carbon doublebond

conversion reaction was detected at 2 s of photoactivation. For the 10, 20, 30, and 40% ethanol groups, the carbon–carbon double-bond conversion reaction was detected at 4, 6, 10, and 15 s, respectively. This demonstrates the effect of the solvent as a retarding agent for the polymerization reaction. It can be theorized that, as the solvent amount increases, the photoinitiator and the density of double-bond terminations in the system, and as a result the reactivity, decreases, explaining the inhibition of the polymerization process. Despite the cited inhibition effect, the final degree of conversion (after 30 s of photoactivation) in the 10 and 20% ethanol groups was higher than the 0% group. This can be explained with Figure 5, which displays the displacement of the R_P^{max} as the ethanol concentration increases, in addition to the Trommsdorf effect attenuation. Although less reactive due to a lower concentration of reactive species, the polymerization reaction from monomer and solvent (protic and aprotic) mixtures displays a larger mobility in the environment, which is favorable to a slower onset of gelation and vitrification.[9]

An alternative to polymerizing methacrylate monomers more efficiently is the use of ternary photoinitiator systems, composed of a dye, an amine, and an onium salt.[11] The DPIHFP presents a good solubility in the methacrylate monomers and its introduction in the photoinitiator system provided a significant increase in polymerization kinetics, as shown in Figures 3 and 4. Although the solvent amount affected the polymerization kinetics, this inhibitory effect in the ternary photoinitiator system was less pronounced than in the binary system. The beginning of the reaction from the 0, 10, 20, 30, and 40% ethanol groups was detected at 1, 3, 3, 6, and 8 s, respectively. Independently of the ethanol concentration, the R_P^{max} from the ternary photoinitiator system (Figure 5) was always higher and more to the left than the binary system.

Two mechanisms can explain the role of an onium salt in the photopolymerization reaction. In this study, the onium salt used (diphenyliodonium hexafluorphosphate) does not absorb at the visible light wavelength,[12] and thus, the cleavage of the C-I bond through the blue light is discarded. However, when an onium salt is used together with a photosensitizer, an increase in the reaction kinetics occurs.[13] CQ, when absorbing blue light, leads to an excited species [CQ]*. This species reacts with an onium salt, forming an exciplex state [Eq. (3)] and the onium salt is reduced by electron transfer [Eq. (4)]. The diphenyliodine free radical formed is unstable and decomposes rapidly into phenyliodine, while a phenyl free radical [Eq. (5)] makes the reaction irreversible. These phenyl reactive species are effective in initiating the polymerization reaction [Eq. (6)]. Radicals generated during the polymerization propagation are effective in cleaving the C-I bond as viewed in Eq. (7), releasing another phenyl radical and starting the polymerization reaction (Scheme 2).

$$[CQ]^{*} + Ph_2I^{+}\,PF_6^{-} \longrightarrow [CQ\bullet\bullet\bullet Ph_2I^{+}\,PF_6^{-}]^{*} \qquad (3)$$

$$[CQ\bullet\bullet\bullet Ph_2I^{+}\,PF_6^{-}]^{*} \longrightarrow [CQ]^{\overset{+}{\bullet}}\,PF_6^{-} + Ph_2I^{\bullet} \qquad (4)$$

$$Ph_2I^{\bullet} \longrightarrow PhI + Ph^{\bullet} \qquad (5)$$

$$Ph^{\bullet} + M \longrightarrow PhM^{\bullet} \qquad (6)$$

$$\sim M^{\bullet} + Ph_2I^{+}\,PF_6^{-} \longrightarrow \sim M^{+}PF_6^{-} + PhI + Ph^{\bullet} \qquad (7)$$

Scheme 2.

It is also suggested that the DPIHFP acts as a catalyst, decreasing the activation energy of the photoinitiation. First, an exciplex between [CQ]* and DPIFHP is formed. This exciplex reacts further with the amine (EDAB), giving a radical amine species. The radical amine initiates the polymerization, regenerating the DPIHFP. This regeneration enables the salt to form another exciplex with a new photoactivated CQ (Scheme 3, Eq (8)).

$$[CQ\bullet\bullet\bullet Ph_2I^+ PF_6^-]^* + \quad R_2NCHR' \longrightarrow [CQ]H + R_2NC^{\bullet}R' + Ph_2I^+ PF_6^- \qquad (8)$$

Scheme 3.

The effect observed from the solvent concentration on the polymerization kinetics should be considered as a significant concern in solvent-based dental adhesives, once they are applied directly on the dentin tissue and are photopolymerized in situ. Moreover, some commercial solvent-based dental adhesives have water as cosolvent besides the dentin moisture, which potentially would be an additional challenge to evaporation. As previously described,[4] even after long air-drying, a significant amount of residual solvent is kept in the monomer.

According to this study, the solvent decreases the polymerization kinetics, consequently, less polymer conversion occurs. In addition to the effect of a lower degree of conversion on the mechanical properties of a polymer that are directly related with bond strength,[3,14] uncured methacrylates are harmful to pulp health.[15] Thus, the use of diphenyliodonium hexafluorphosphate as a third component in the photoinitiation system appears to be an interesting alternative to improve the degree of conversion and biocompatibility of dental adhesive polymers. With the best of author’s knowledge, there are no reports about diphenyliodonium biocompatibility. The toxicity of diphenyliodonium salts derivatives using fibroblast 3T3 cell culture is under investigation by the authors.

Additionally, two points need to be highlighted. (1) Even with the addition of DPIHFP, when the solvent-free monomer blend was polymerized, it reached a higher degree of conversion at 10 s when compared with any other ethanol concentration; (2) the degree of conversion alone does not predict the long-term durability of the bonding interface, even with a higher conversion, as any residual solvent can introduce critical defects in the polymer structure, affecting its performance.[16]

3.6 CONCLUSION

The polymerization kinetics of a model dental adhesive resin improved with the use of a ternary photoinitiation system, which showed to be less sensitive to the presence of residual solvent before photoactivation.

3.7 ACKNOWLEDGEMENT

The authors were grateful to CAPES for the scholarship and to Esstech Inc for the donation of the reagents.

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4. ARTIGO 3*

Título: Onium salt increases bond strength stability of a model self-etching adhesive

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4.1 Abstract

The aim of this study was to evaluate the influence of an onium salt on the immediate and long term microtensile bond strength of experimental dental adhesive systems. A monomer blend based on Bis-GMA, TEGDMA, and HEMA was used as a model dental adhesive resin, which was polymerized using two binary systems camphorquinone (CQ) plus ethyl 4-dimethylamine benzoate (CQ+EDAB) and, CQ plus diphenyliodonium hexafluorphosphate (CQ+DPIHFP) and a ternary system (CQ+EDAB+DPIHFP). Additionally, a model self-etching primer was formulated for the bonding procedure. Clearfil SE Bond (CSEB) was used as a commercial reference. One hundred bovine incisors were prepared for the microtensile bond strength (µTBS) test with restorations by the incremental technique, photoactivated for 20s. After 24h storage in distilled water at 37℃, beams with an area of 0 .5mm^2 were produced and the µTBS was measured in MPa, in a universal testing machine. For each experimental group, 10 teeth were used to obtain 20 beams for each time evaluated, 24 hours or one year storage. Bond failure pattern was analyzed with an optical microscope (500x). Two-way ANOVA and Student-Newman-Keuls' post-hoc test were used to compare means of groups ($\alpha=5\%$). After one year of storage, the µTBS values of the group CQ+EDAB+DPIHFP showed significantly higher bond strength ($p<0.05$) than CQ, CQ+DPIHFP and CQ+EDAB groups and no difference from CSEB group. The ternary photoinitiation system with DPIHFP maintained increased bond strength to dentin of model self-etching adhesive systems after one year of aging.

Keywords: photo-initiators, camphorquinone, diphenyliodonium hexafluorphosphate, tertiary amine, dental adhesive, bond strength.

4.2 Introduction

Diaryliodonium salts are efficient photoinitiators for cationically mediated polymerization [1]. Most of these photoinitiators are active when irradiated in a light range below 300 nm, therefore, UV light sources are used. Although this activation strategy is satisfactory in some applications, such as paints and coatings, the use of UV light is not recommended in the biological field. However, the use of dyes as sensitizers that absorb in the visible light region allows the reaction with the onium salts, promoting decomposition of free radicals suitable for the polymerization process.[2-4].

In the development of dental adhesives, can be listened important reasons to use an onium salt: Water-solubility, due its ionic character that can promote the polymerization of hydrophilic monomers in dental adhesives avoiding phase separation of adhesive[5]; compatibility with epoxy-based resin composites [6] and the significant increase in the rate of free radical polymerization [4] due to its ability to increase the reactivity of free radical cure [7]. Additionally onium salts increases the rate of polymerization of dental adhesive resins [4], which is very important in systems that require a fast cure, such as dental adhesives, and also reduces the inhibitory polymerization effect of an organic solvent in a model dental adhesive resin [8].

Therefore, it was hypothesized that adhesive systems with the addition of a ternary photoinitiator system including dye (camphorquinone), tertiary amine and an onium salt could immediately and longitudinally improve bond strength, by the obtainment of a quality and durable polymer. The aim of this study was to evaluate the influence of an onium salt on the immediate and long term microtensile bond strength to dentin of experimental dental adhesive systems.

4.3 Material and Methods

4.3.1 Materials

The monomers used in this study were bisphenol A glycol dimethacrylate (Bis-GMA), triethylene glycol dimethacrylate (TEGDMA) and 2-hydroxyethyl methacrylate (HEMA) and camphorquinone (CQ), provided by Esstech Inc, USA; Ethyl 4-dimethylaminobenzoate (EDAB) and diphenyliodonium hexafluorphosphate (DPIHFP) were purchased from Aldrich Chemical Co (Milwaukee, WI, USA) and used without further processing. To perform the monomer light activation, a halogen light-activation unit (XL 3000, 3 M ESPE, St. Paul, MN, USA) was used and the irradiation value (650 mW/cm2) was confirmed with a digital power meter (Ophir Optronics, Danvers, MA, USA). The Clearfil SE Bond (CSEB) adhesive system was used as a control.

4.3.2 Formulations

The model self-etching adhesive system was formulated in two steps: adhesive resin and self-etching primer. The model dental adhesive resin was formulated by mixing 50wt. % Bis-GMA, 25wt. % TEGDMA, and 25wt. % HEMA. Four initiator systems, with the reagents shown in Figure 1, were investigated at various levels: 1mol% of CQ; 1mol% of CQ + 1mol% DPIHFP; 1mol% of CQ + 1mol% EDAB; 1 mol% CQ + 1 mol% EDAB + 1mol% DPIHFP. No radical scavenger was added. Additionally, a model self-etching primer was produced, based on HEMA, phosphate monomers and solvents. All formulations were weighed on an analytical balance (AG 200, Gehaka , Brazil), manually mixed in a beaker and left in an ultrasonic cleaner (CBU 100 / 1LDG, PlanaTC, Tatuapé, SP, Brazil) for 10 minutes.

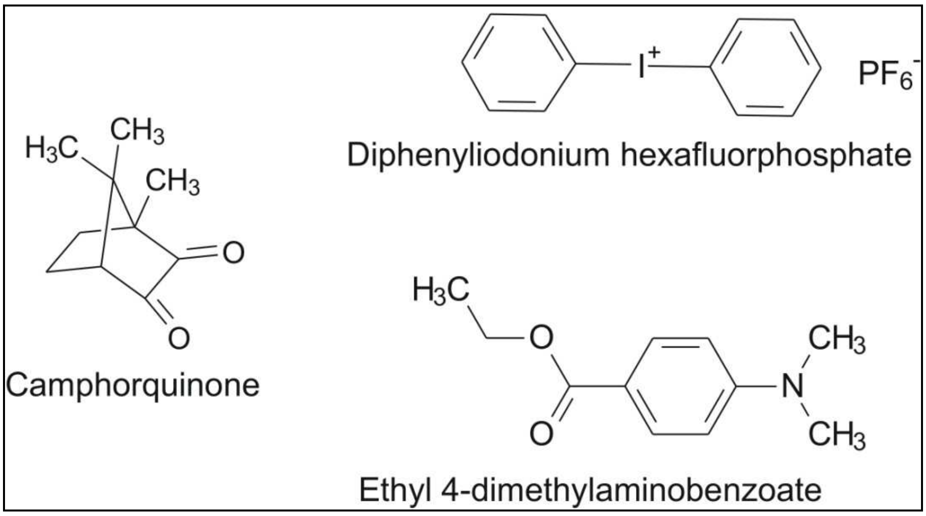

Figure 1. Molecular structure of the photoinitiator and co-initiators used in the experimental adhesives evaluated.

4.3.3 Microtensile Bond Strength Test

Fifty freshly extracted mandibular bovine incisors were cleaned and stored in a 0.5 wt% Chloramine T solution for 1 week and had their buccal enamel trimmed to expose the superficial dentin. To achieve a standardized smear layer the dentin surfaces were polished under irrigation, with 600 grit SiC paper for 1 minute at 100 rpm (Aropo l- E, Arotec S.A. Indústria e Comércio, Cotia, SP, Brazil). After rinsing, the teeth were randomly divided into five groups according to the adhesive systems, totaling 10 teeth per group. The self-etching primer was actively applied on the dry dentin surface for 30 s and was air-dried for solvent evaporation for 10 s. One coat of adhesive resin was applied and light activated for 20 s each. After adhesive light activation, increments of resin composite were inserted to cover the dentin surface completely, until the restoration was 4 mm high. Each increment was smaller than 2 mm and was light activated for 20 seconds. The commercial adhesive system CSEB was applied in accordance with the manufacturer's recommendations.

After storage in distilled water at 37 ℃ for 24 h, the teeth were sectioned perpendicular to the bonded interface, with a cooled diamond saw at low speed (Isomet, Buehler Ltd, Lake Bluff, IL). Beams with a cross-sectional surface area of approximately 0.5 mm^2 were produced and measured with a digital caliper (Digimatic Caliper 500-

144B, Mitutoyo Sul Americana, Suzano, SP, Brazil) for microtensile bond testing. For each group, 20 beams were stored in distilled water at 37℃ for evaluation after 1 year. After storage, the beams had their ends fixed to a microtensile test device, using a cyanoacrylate adhesive. The microtensile test was performed in a universal test machine Emic DL-500 (Emic, São José dos Pinhais, Brazil) at a crosshead speed of 0.5 mm/min. Bond strengths were calculated in MPa and analyzed by two-way ANOVA (photoinitiator system and storage time) and Student-Newman-Keuls as post hoc test at the 0.05 level of significance.

The fragment corresponding to dentin in each beam was removed from the device and dehydrated in silica gel for 24 h at room temperature. All specimens were analyzed under optical microscope at 100x and 500x magnification, and failure modes were classified as adhesive, cohesive in dentin, cohesive in adhesive, mixed and cohesive in resin.

4.4 Results

After formulating the model adhesive resins, stable systems were obtained and the immediate and longitudinal µTBS values, in MPa, are shown in Table 1.

Table 1. Mean and standard deviation values of microtensile bond strength (µTBS), in MPa, of the photoinitiation systems tested.

Groups	**µTBS Mean** (± standard deviation)	
	24 hours	**1 year**
CQ	29.1 (8,1) A c	16.8 (11.3) B c
CQ+ DPIHFP	36.3 (13,8) A bc	18.6 (23.3) B c
CQ+EDAB	46.1 (11,1) A ab	41.4 (16.6) A b
CQ+ DPIHFP +EDAB	57.7 (12,4) A a	57.6(22.0) A a
CSEB	52.2 (11,5) A a	49.7 (13.7) A ab

Abbreviations: CQ: camphorquinone, DPIHFP: diphenyliodonium hexafluorphosphate, EDAB: Ethyl 4-dimethylaminobenzoate, CSEB: Clearfil SE Bond (Kuraray). Values followed by different lower case letters in columns shows statistical differences for photo-initiation system ($p<0.05$). Values followed by different upper case letters in lines shows statistical differences for time ($p<0.05$).

The immediate (24h) bond strength of ternary photo-initiation systems (CQ + DPIHFP + EDAB) showed no significant difference from those of the CSEB and CQ+EDAB groups ($p>0.05$) and was significantly higher than those of CQ and CQ+DPIHFP ($p<0.05$). No significant differences in bond strength values were showed among the binary (CQ+EDAB and CQ+ DPIHFP) system groups and CQ group ($p>0.05$).

After 1 year of aging, µTBS values of the CQ and CQ+DPIHFP groups significantly decreased when compared with the immediate values. However, the ternary photoinitiation system (CQ+EDAB+DPIHFP), the binary photoinitiation system (CQ+EDAB) and CSEB groups showed no significant decrease in the longitudinal test. In the 1-year comparison, the ternary system once again showed no significant difference in bond strength from CSEB group and the value was significantly higher than those of the binary systems (CQ+DPIHFP and CQ+EDAB) groups and CQ group ($p<0.05$).

The failure pattern of debonded specimens is shown in Figure 2. The mixed failure pattern was predominant for all groups and in both periods of time. At 1 year, an increase in the cohesive dentin pattern was observed for CSEB and ternary photoinitiation system (CQ+DPIHFP+EDAB) groups.

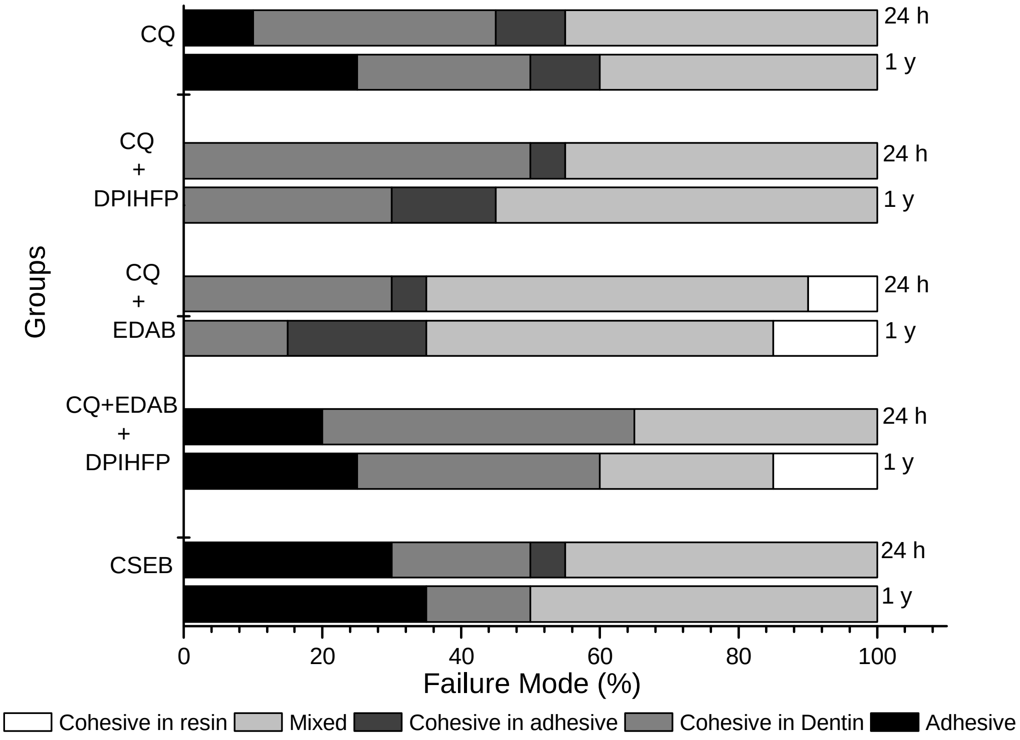

Figure 2. Failure pattern of debonded specimens at 24 hours (24 h) and 1 year (1 y).

4.5 Discussion

Efficient bond to tooth substrate depends on immediate and long-term bond strength at the adhesive dentin interface [9]. The adhesive system monomers penetrate into dentin substrate in the presence of water, collagen and residual organic solvents. In this environment, adverse to polymerization reaction, the degree of conversion of the polymer layer formed is a concern as regards bond strength longevity [10]. Since the degree of conversion is strongly related to the mechanical properties of the polymer formed [11], it is of extreme importance to evaluate the microtensile bond strength of different photoinitiator systems contained in experimental dental adhesive systems.

Dental methacrylate monomers containing a photoinitiator dye, such CQ, are commonly polymerized by exposure to light. CQ is an α-dicarbonyl compound that becomes a reactive specie after light absorption and photolysis. When used alone, the reactive species from CQ can easily recombine, leading to the cage effect due molecule regeneration [12]. Therefore, polymers formed in this way, using CQ only, have a low degree of conversion [4], which could explain the low immediate and longitudinal bond strength of CQ group.

CQ is a photoinitiator that needs a second component for effective radical generation. Tertiary amines are very effective in reacting with the excited CQ* species as an H-donor to generate free radicals that can start the polymerization process [13]. Addition of a tertiary amine (EDAB) enhances the rate of polymerization and degree of conversion of comonomer blends [4], leading to enhanced immediate bond strength and maintaining it after 1 year of aging in the binary system CQ+EDAB group. These systems that use CQ and tertiary amines are called binary photoinitiation systems and are the most frequently used in currently available dental adhesives. Another binary system in which the tertiary amine (EDAB) was replaced by the onium salt (DPIHFP) was used in this study. However, the CQ+DPIHFP group showed decreased bond strength longitudinally, which could be explained by the low rate of polymerization of this system [4].

An alternative to enhance methacrylate polymerization is the use of a ternary photoinitiator system with a dye (CQ), a tertiary amine (EDAB) and an onium salt (DPIHFP). Although diphenyliodonium hexafluorphosphate (DPIHFP) has no absorption at the visible light wavelength, and cleavage of the C-I bond through blue light is not possible, its association with a photosensitizer allows an increase in polymerization reaction [2-4]. Two mechanisms to explain the role of DPIHFP as a catalyst to the polymerization reaction were proposed elsewhere [8]. After formation of the exciplex between DPIHFP and CQ, a reaction of this complex with tertiary amine promotes the regeneration of onium salts. The regenerated DPIHFP could react with non reacted CQ molecules producing new exciplex states. Since the number and proportion of free radicals formed are of extreme importance in the polymerization reaction, the addition of the onium salt could decrease unreacted monomers and increase the mechanical properties of the polymer formed (8).

In this study, the ternary group (CQ+EDAB+DPIHFP) maintained the high bond strength values during the evaluated time, promising enhanced longitudinal bond strength when compared with binary photoinitiator systems (CQ+EDAB and CQ+DPIHFP). An enhanced polymerization rate is related to the high degrees of conversion and cross-linking densities of dental adhesive polymers [14,15]. Moreover, the polymerization rate, degree of conversion and hardness depend on the photoinitiator type [16].

Considering that the mechanical properties of the hybrid layer components play an important role in adhesion to tooth substrate, the durability of these components is correlated with the durability of the resin–dentin interface [17]. In fact, some studies have shown that dental adhesives components demonstrated lower mechanical properties when specimens were stored in water for 6 months[18] and for 1 year [19].

One of the mechanisms that explain the reduction in bonding durability is the effect of water in the bonding agent network and the dissolution of some components[7]. Water uptake by the hybrid layer could produce a relaxation process that leads to a separation of polymer chains, promoting polymer swelling followed by chain disentanglement and dissolution, decreasing its mechanical properties. After separation of the polymer chains, unreacted monomers and oligomers trapped in the polymer network are released through porosities and nano-sized voids [20] leading to degradation of the material. In addition, these leached monomers could diffuse through dentin tubules and may produce a cytotoxic effect on pulp cells [21,22].

Addition of the onium salt as a polymerization reaction catalyst with an ionic character could promote the polymerization of hydrophilic monomers[7] avoiding the occurrence of phase separation and decrease polymerization inhibition by residual organic solvents [8]. With a higher degree of conversion, a more biocompatible adhesive system and a more durable bond is expected due to the decrease of residual unpolymerized monomers and increased cross-linking density, respectively.

It has been observed that the adhesive resin is the weakest component of the resin–dentin interface [23]. However, the predominant failure pattern observed in fracture analysis in this study was mixed. No adhesive failure and few cohesive failures in adhesive resin were verified for the ternary photoinitiator system group (CQ+EDAB+DPIHFP) and CQ+EDAB binary system group. Theoretically, alterations in adhesive resin to enhance mechanical properties can directly influence the bond strength of the resin- dentin interface. It was suggested that such an interface with infiltrated dentin may achieve strengths close to that of mineralized dentin [23], which could explain the results of failure pattern analysis.

Although most of the adhesive systems presented an acceptable immediate performance [24], the long-term durability of dentin/resin interfaces is a concern. In this study, the ternary photo-initiation system with DPIHFP maintained bond strength to dentin of model self-etching adhesive systems after one year of storage. The increased degree of conversion and polymerization rate promoted by the addition of an onium salt produced a hybrid layer and adhesive layer with enhanced cross-linking and mechanical properties, increasing bond strength to the dentin substrate. In addition, polymerization of hydrophilic monomers, such as 2-hydroxyethylmethacrylate, could have prevented phase separation from occurring, thereby decreasing hydrolytic degradation during the storage period. Adhesive systems with decreased degradation have fewer leachable components, thereby increasing their biocompatibility with oral tissues and enhancing their clinical performance.

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5. CONCLUSÃO FINAL

O sal de iodônio hexafluorfosfato de difeniliodônio demonstrou ser um efetivo coiniciador para a polimerização radicalar fotoiniciada de metacrilatos. Considerando as condições dos experimentos realizados, sua utilização promoveu um expressivo aumento na velocidade da reação de polimerização. Quando introduzido na resina adesiva de um adesivo odontológico, promoveu um melhor desempenho do material, tanto imediatamente após aplicação, quanto após um ano de envelhecimento da interface adesiva.

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