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EDUARDO JOSÉ CARVALHO DE SOUZA JUNIOR

INFLUÊNCIA DE FOTOINICIADORES ALTERNATIVOS NA DURABILIDADE DA UNIÃO, ADAPTAÇÃO MARGINAL E PROPRIEDADES FÍSICO-QUÍMICAS DE RESINAS ADESIVAS EXPERIMENTAIS FOTOATIVADAS POR LEDS

INFLUENCE OF ALTERNATIVE PHOTOINITIATORS ON BOND DURABILITY, MARGINAL ADAPTATION AND PHYSICAL-MECHANICAL PROPERTIES OF EXPERIMENTAL ADHESIVE RESINS PHOTOCURED BY LEDS

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UNIVERSIDADE ESTADUAL DE CAMPINAS
FACULDADE DE ODONTOLOGIA DE PIRACICABA

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Tese apresentada à Faculdade de Odontologia de Piracicaba da Universidade Estadual de Campinas como parte dos requisitos exigidos para a obtenção do título de Doutor em Materiais Dentários.
Thesis presented to the Piracicaba Dental School of the University of Campinas in partial fulfillment of the requirements for the degree of Doctor in Dental Materials.

Orientador: Mario Alexandre Coelho Sinhoreti
Este exemplar corresponde à versão final da tese defendida
por Eduardo José Carvalho de Souza Junior e orientada pelo
Prof. Dr. Mario Alexandre Coelho Sinhoreti

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Resumo

O objetivo neste estudo foi analisar o efeito de diodos emissores de luz (LEDs) nas propriedades físicas, químicas, resistência da união (RU), adaptação marginal (AM) e na durabilidade de restaurações realizadas com adesivos experimentais contendo diferentes fotoiniciadores. Uma resina modelo contendo uma mistura de BisGMA/HEMA (60/40 em peso) e dimetil amino etil metacrilato (co-iniciador) foi preparada com os diferentes fotoiniciadores: CQ (Canforoquinona), PPD (1-Fenil-1,2-Propanodiona) e BAPO (Óxido bis-alquil fosfínico), além da associação entre eles. As amostras foram fotoativadas por duas fontes de luz LED, uma de 2° geração (Radii Cal, SDI) e outra de 3° geração (Bluephase G2, Ivoclar Vivadent). A irradiância foi aferida a partir de medidas em potênciômetro e a densidade energética foi padronizada em 48J/cm^2. As propriedades avaliadas foram o grau de conversão (GC), cinética de polimerização (CI), análise da permeabilidade dentinária (PMD), sorção (SO) e solubilidade (SL), resistência flexural (RF), módulo flexural (MF) e amarelamento (YL). Para o teste de RU, o ensaio de microtração foi realizado em dentina plana de 70 molares humanos, avaliados após 24 horas e após 1 ano de armazenamento em água a 37ºC. A AM foi mensurada por meio de réplicas das margens superficial e interna de 70 molares humanos, analisadas em microscopia eletrônica de varredura (MEV). Os ensaios de GC, PMD, SO, SL, RF, MF e AM foram submetidos à análise de variância dois fatores, enquanto a RU foi submetida à análise de variância dois fatores (fotoiniciadores e fontes de luz), com medidas repetidas no tempo. Após, todas as médias foram comparadas pelo teste de Tukey (α = 5%). Os adesivos contendo os fotoiniciadores alternativos, em especial BAPO e BAPO/amina monstraram maior potencial de polimerização, evidenciado pela cinética de conversão. Ainda, os fotoiniciadores alternativos promoveram melhor selamento dentinário, sorção e solubilidade similares e propriedades físico-químicas com melhor desempenho quando comparados aos adesivos convencionais contendo CQ. Em relação à resistência de união, os adesivos contendo BAPO promoveram os melhores desempenhos em até um ano de degradação hidrolítica.

Palavras-chave: Adesivos dentais; fotoiniciadores; fotoativação.

Abstract

The aim of this study was to evaluate the effect of light emitting diodes (LEDs) on the physical-chemical properties, bond strength (BS) and marginal adaptation (MA) of experimental adhesives containing diferent photo-initiators. A model resin containing a mixture of BisGMA/HEMA (60/40 wt%) and DMAEMA (co-iniciator) was prepared using different photo-initiators: CQ (Camphorquinone), PPD (1-Phenyl-1,2-Propanedione) e BAPO (Bisalquylphosphine oxide) and their association. The specimens were photoactivated by two LEDs, one monowave (Radii Cal, SDI) and other polywave (Bluephase G2, Ivoclar Vivadent). Irradiance was measured in potenciometer and the energy dose was standardized. The following properties were analyzed: degree of conversion (DC) and for the curing kinetics (CI), dentin permeability (DPM), water sorption (SO), water solubility (SL), flexural strength (FS), flexural modulus (FM) and yellowing (YL). For the BS test, the microtensile test was realized in 70 molars with planned dentin, immediately or after 1-year of water storage. The MA, superficial and internal marginal adaptation measurements were realized by epoxy replicas of the bonded margins using the scanning eléctron microscopy. DC, DPM, SO, SL, FS, FM and AM were submitted to a two-way ANOVA and BS to a two-way repeated measurement ANOVA. Next, the analyzes were submitted to the Tukey's test ($\alpha = 5\%$). The adhesives containing the alternative photoinitiators, such as BAPO and BAPO/amine showed a higher curing potential, promoted by the curing kinetics. Moreover, these alternative photoinitiators showed a better dentin sealing, with similar sorption and solubility values and high physical-mechanical properties when compared to the other groups based in CQ. In relation to the bond strength, the BAPO containing adhesives promoted higher performance even after 1-year of hydrolytic degradation.

Keywords: Dental adhesives; photoinitiators; photoactivation.

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INTRODUÇÃO

O avanço da odontologia adesiva tem proporcionado o desenvolvimento de técnicas restauradoras mais conservadoras, além de proporcionar uma união efetiva dente/restauração (Asmussen e Peutzfeldt, 2003; Cunha *et al.*, 2008; Alonso *et al.* 2007). Para tanto, os sistemas adesivos de 3 passos que utilizam o condicionamento ácido do esmalte e da dentina são considerados o padrão-ouro para a adequada união dos materiais resinosos ao substrato dental, devido à menor permeabilidade fornecida pela dentina hibridizada e menor degradação da união, além de maior resistência da união (Brackett *et al.*, 2008; Perdigão, Lopes e Gomes, 2008).

As resinas adesivas atuais são fotoativadas por luz visível, dentro da faixa azul do espectro e utilizam geralmente uma di-cetona como fotoiniciador (canforoquinona-CQ), juntamente com uma amina terciária como co-iniciador (Taira *et al.*, 1988; Krishnan & Yamuna, 1998; Neumann *et al.*, 2005). A CQ possui coloração amarelada, além de poder proporcionar alguns efeitos adversos, como genotoxicidade (Nomura *et al.*, 2006) e, por isso, é incorporada em pequena quantidade na matriz (Cook & Chong, 1985; Park *et al.*, 1999; Neumann *et al.*, 2005). Ao absorver luz visível entre 400-500nm, a CQ atinge um estado de excitação e se combina com um agente redutor contido na matriz orgânica, para gerar os radicais livres responsáveis pelo início da reação de polimerização. Por essa razão, um agente redutor (um doador de elétrons) é adicionado aos adesivos dentais ativados pela luz visível. Dos diferentes agentes redutores ou co-iniciadores, os mais reativos são as aminas terciárias, seguidas das aminas secundárias, enquanto as aminas primárias são quase não reativas (Cook, 1992; Rueggeberg, 1999; Stansbury, 2000; Neumann *et al.*, 2006).

Atualmente, alguns compósitos, especialmente nas cores mais claras, utilizam sistemas fotoiniciadores ou co-iniciadores alternativos como o PPD (Fenil Propanodiona), Lucirin TPO (Óxido mono-alquil fosfínico ou BAPO (Óxido bis-alquil fosfínico), tendo em vista o fato de a canforoquinona apresentar cor amarela, o que pode vir a comprometer as propriedades estéticas do compósito (Sun & Chae, 2000; Asmussen & Peutzfeldt, 2002; Emami & Soderholm, 2005; Neumann *et al.*, 2006; Ogunyinka *et al.*, 2006; Albuquerque *et al.*, 2013). Para os sistemas adesivos, somente alguns trabalhos avaliaram o comportamento de diferentes fotoiniciadores, como o TPO e o BAPO (Ikemura *et al.*, 2008; Ikemura e Endo; 2010; Cadenaro *et al.*, 2010, Brandt *et al.*, 2010). Esses autores observaram que esses fotoiniciadores também possibilitam iniciar a reação de polimerização de resinas dentais, mesmo sem o conteúdo de amina terciária na formulação desses materiais. Alguns fotoiniciadores alternativos, como o PPD, possuem uma reação de foto-clivagem, que gera maior quantidade de ligações cruzadas no polímero formado, mesmo possuindo velocidade de reação mais lenta, podendo levar ainda à menor tensão na interface dente-restauração (Park *et al*, 1999; Brandt *et al.*, 2013).

No entanto, diferentemente da CQ, estes fotoiniciadores são ativados por comprimentos de onda menores, na região do ultravioleta/visível (UV-Vis) (Stansbury, 2000; Brandt *et al.*, 2013). Como o espectro de emissão de uma fonte de luz possui forte influência no desempenho de fotoativação, especialmente quando diferentes sistemas de fotoativação são comparados (Uhl *et al.*, 2003; Uhl *et al.*, 2004), os fotoiniciadores CQ e PPD são preferidos, pois possuem maior correlação com as fontes de luz usadas atualmente na odontologia, uma vez que muitas das propriedades exibidas por uma resina adesiva fotoativada são dependentes da correlação entre a distribuição do espectro emitido pela fonte de luz e a máxima absorção pelo fotoiniciador (Stahl *et al.*, 2000; Neumann *et al.*, 2005; Neumann *et al.*, 2006). Relativamente novos no mercado odontológico, os aparelhos de fotoativação que utilizam luz emitida por diodos (LEDs) foram introduzidos para a fotoativação de compósitos restauradores (Kurachi *et al.*, 2001; Uhl *et al.*, 2005; Schneider *et al.*, 2006). Os LEDs são constituídos de materiais semicondutores que determinam o tipo de luz emitida (Bennett & Watts, 2004). Cada semicondutor apresenta uma faixa de energia que determina o espectro de emissão da luz, caracterizando a cor emitida. Para fotoativação de compósitos odontológicos, os LEDs emitem luz azul. A utilização dos LEDs se justifica pelo fato destes possuírem longo tempo de vida útil (acima de 10.000 horas), pouca degradação com o passar do tempo e não necessitarem de filtros especiais devido ao estreito espectro de comprimento de onda emitido, que na maioria das vezes coincide com o pico de absorção da canforoquinona, ou seja, próximo de 468 nm (Schneider *et al.*, 2006; Brandt *et al.*, 2010).

Algumas fontes de luz contendo LEDs emitem irradiação na região abaixo de 410nm para ativar os fotoiniciadores, ou co-iniciadores, que absorvem luz nesta região (Price *et al.,* 2005). Dessa forma, podem ser uma alternativa para a ativação de fotoiniciadores que absorvam luz em comprimentos de onda na região UV-Vil (Ultra Violeta-Visível).

Novas formulações de adesivos contendo fotoiniciadores alternativos, como o PPD e o BAPO, sozinhos ou em associação com a canforoquinona são importantes no intuito de avaliar o desenvolvimento de adesivos com melhores propriedades físico-químico-mecânicas comparado aos adesivos convencionais somente à base de canforoquinona, melhorando seu comportamento estrutural e em uso quando aplicados em restaurações dentais. Além disso, o amarelamento causado pela cor intrínseca da canforoquinona, presente em sistemas adesivos, especialmente em algumas situações de restauração de dente anterior previamente clareado, pode comprometer a estética dessas restaurações, formando uma linha amarelada na interface entre dente e restauração. Neste caso, o desenvolvimento de adesivos com menor concentração de canforoquinona e adição ou substituição por PPD ou BAPO pode favorecer a um resultado estético final mais satisfatório, adicionalmente a melhores propriedades do material resinoso.

Dessa forma, torna-se interessante avaliar o efeito de diferentes fontes de luz LED, nas propriedades físico-químico-mecânicas, durabilidade da união e adaptação marginal de adesivos dentais experimentais contendo diferentes sistemas fotoiniciadores. A partir dessa análise, será possível avaliar a viabilidade de formulação de adesivos contendo fotoiniciadores alternativos, para melhorar as propriedades intrínsecas do material e seu comportamento quando utilizadas para união à estrutura dental.

Devido ao fato da qualidade dos adesivos dentais fotoativados estar diretamente relacionada às características da matriz polimérica, e essas características serem influenciadas pelo tipo de luz e fotoiniciador utilizados para a ativação, este estudo tem como objetivo avaliar resinas adesivas contendo diferentes sistemas fotoiniciadores (CQ, PPD e BAPO) fotoativadas por duas fontes de luz LED (um LED de poliondas e outro de pico único). Foram avaliadas as seguintes propriedades físico-químicas:

- Grau de conversão
- Cinética de polimerização
- Resistência flexural
- Módulo flexural
- Amarelamento
- Sorção de água
- Solubilidade em água
- Durabilidade da união
- Permeabilidade dentinária
- Adaptação marginal

O presente trabalho está apresentado no formato alternativo de tese de acordo com as normas estabelecidas pela deliberação 002/06 da Comissão Central de Pós-Graduação da Universidade Estadual de Campinas. Assim está disposto em 4 capítulos:

Capítulo 1 – Curing kinetics of dental adhesives blends containing different photo-initiators cured by single-peak and polywave LEDs;

Capítulo 2 – Effect of PPD and BAPO on the physical-mechanical properties and marginal adaptation of dental adhesives;

Capítulo 3 – Dentin permeability and sorption/solubility parameters of experimental dental adhesives containing alternative photo-initiators; e,

Capítulo 4 – Long-term dentin bond durability of experimental three-step dental adhesives containing phenylpropanedione and bisalquylphosphine oxide cured by LEDs.

CAPÍTULO 1

Curing kinetics of dental adhesives blends containing different photo-initiators cured by single-peak and polywave LEDs

Abstract

The aim of this study was to evaluate the curing kinetics, degree of conversion (DC) and maximum rate of polymerization (RPmax) of experimental adhesives containing alternative photoinitiators. Experimental hydrophobic adhesive resins containing BisGMA/HEMA as organic matrix were manipulated, with different photoinitiator content: G1- CQ/amine, G2- PPD/amine, G3- CQ/PPD/amine, G4- BAPO/Amine, G5- BAPO, G6- CQ/BAPO/Amine, G7- PPD and G8- the hydrophobic resin of Adper Scotchbond Multi-Purpose as control. 3µL of each adhesive was dispensed on the diamond cristal of the FTIR-ATR device and cured with a polywave LED (Bluephase G2) and a monowave LED (Radii-Cal), 48J of energy dose. The curing kinetics was monitored for 5 minutes and then the DC at 5 minutes and RPmax were obtained for each adhesive (n=7). Data were submitted to two-way ANOVA and Tukey's test at a pre-set alpha of 0.05. The BAPO, BAPO/amine and the control adhesives showed higher DC values compared to the other resins. The PPD alone presented the lowest DC (2.9%). The adhesives containing PPD/amine or CQ/amine showed similar monomer conversion. In conclusion, CQ can be replaced by BAPO and PPD/amine in hydrophobic adhesive resins, since it can increase the degree of conversion and the rate of polymerization of these restorative materials.

Keywords: monomer conversion, light curing unit, dental adhesive.

Introduction

Conventionally, etch-and-rinse adhesives have been widely used in direct and indirect restorations. This category of adhesive can be available in three-step and a two-step protocol, depending if the primer and bonding resin are presented in the same bottle or in different ones (Loguercio *et al.*, 2014). The three-step etch-and-rinse has been considered the clinical gold standard in dental bonding (Peumans *et al.*, 2005; De Munk *et al.*, 2005), especially due to the application of a hydrophobic resin coating. This neat resin layer is responsible for better *in vitro* and *in vivo* performance than the one-bottle etch-and-rinse adhesives (Armstrong *et al.*, 2003).

The conventional dental adhesive systems are mostly light-cured resins. The light curing units (LCUs) should guarantee a satisfactory monomer conversion of the adhesive and the light emitting diodes (LEDs) have been shown to effectively cure dental adhesives, emitting unfiltered blues and/or violet light (Asmussen 2002; Faria-e-Silva *et al.*, 2010). Some adhesive systems are not well cured with monowave LEDs (Faria-e-Silva *et al.*, 2010) due to alterative photoinitiators content; to overcome this problem, polywave third generation LEDs were introduced (Brandt *et al.*, 2010; Price *et al.*, 2010) in order to deliver additional light output at the UV-Vis region of the electromagnetic spectrum (400 - 415 nm). The second peak in the UV-VIS region may promote a satisfactory cure of these adhesives, containing alternative photoinitiators systems, such as phenyl propanedione (PPD), bis-alquyl phosphinic oxide (BAPO) (Brandt *et al.*, 2010).

Most of the three-step etch-and-rinse adhesives are formulated with a binary photo-initiator system (camphorquinone as the initiator combined to a tertiary amine as co-initiator, CQ/amine). Therefore this conventional photo-initiator system has some drawbacks, such as strong yellow coloration compromising aesthetic properties

(Albuquerque *et al*., 2013), low polymerization rate and efficiency, needing the presence of a amine co-initiator which could affect the biocompatibility and be oxidized over time (Cadenaro *et al*., 2010; Schroeder & Vallo, 2007). So, in order to overcome these shortcomings, alternative photo-initiator systems such as phenyl-propanedione (PPD) and phenylbis(2,4,6-trimethylbenzoyl)phosphine oxide (BAPO) have been investigated (Brandt *et al*., 2013; Albuquerque *et al*., 2013).

Although recent studies have proved that the polymerization behavior of dental monomers is beneficial when the aforementioned components are used (Albuquerque *et al*., 2013; Brandt *et al*., 2013), little information exists about the curing kinetics of three-step etch-and-rinse adhesives containing alternative photo-initiators. The aim of this study was to evaluate the curing kinetics (CK), degree of conversion (DC) and maximum rate of polymerization (Rpmax) of adhesives blends containing different photoinitiator systems and photoactivated by a monowave or a polywave LED. The first hypothesis tested was that alternative photoinitiators, such as PPD and BAPO, would have higher polymerization performance than the conventional CQ/AMINE system. The second hypothesis tested was that the polywave LED should provide a better curing performance for the adhesives containing the alternative photoinitiator systems.

Materials and Methods

Resin Preparation

Seven experimental hydrophobic adhesive formulations were tested in this study. The resin matrix for all adhesive formulations consisted in a combination of bisphenol glycidyl methacrylate – 60.0 wt% (BisGMA – Sigma-Aldrich Inc, St Louis, MO, USA); hydroxyethyl methacrylate – 40.0 wt% (HEMA - Sigma-Aldrich Inc, St Louis, MO, USA).

The only difference among the adhesive blends was the photoinitiator system: camphorquinone (CQ), 1-phenyl-1,2-propanedione (PPD) or phenylbis(2,4,6-trimethylbenzoyl)phosphine oxide (BAPO). The photoinitiators were added to the matrix using the same molar concentration (1 mol %). The dimethylaminoethyl methacrylate (DMAEMA - Sigma-Aldrich Inc, St Louis, MO, USA) was used as co-initiators in the proportion 1:1 in some adhesive blends, as shown bellow: G1- CQ/DMAEMA; G2 – PPD/DMAEMA; G3- CQ/PPD/DMAEMA; G4 – BAPO/DMAEMA; G5 – BAPO; G6 – CQ/BAPO/DMAEMA; G7 – PPD; G8 – The hydrophobic resin from Adper Scotchbond Multi Purpose (used as control).

Light curing units (LCUs)

In the present study were used one monowave LED (Radii-Cal, 800 mW/cm^2, SDI, Victoria, Australia) and one polywave LED (Bluephase G2, 1200 mW/cm^2, Ivoclar Vivadent, Schaan, Liechtenstein). The output power (mW) of each LCU was measured using a calibrated power meter (Ophir Optronics, Har-Hotzvim, Jerusalém, Israel). Then, the irradiance (mW/cm^2) was calculated by dividing the output power by the tip area. The spectral distributions of the LCUs were obtained using a spectrometer (USB2000, Ocean Optics, Dunedin, FL, USA). These data (irradiance and spectral distribution) were integrated by using the Origin 6.0 software (OriginLab Northampton, MA, USA) as shown in Figure 1.

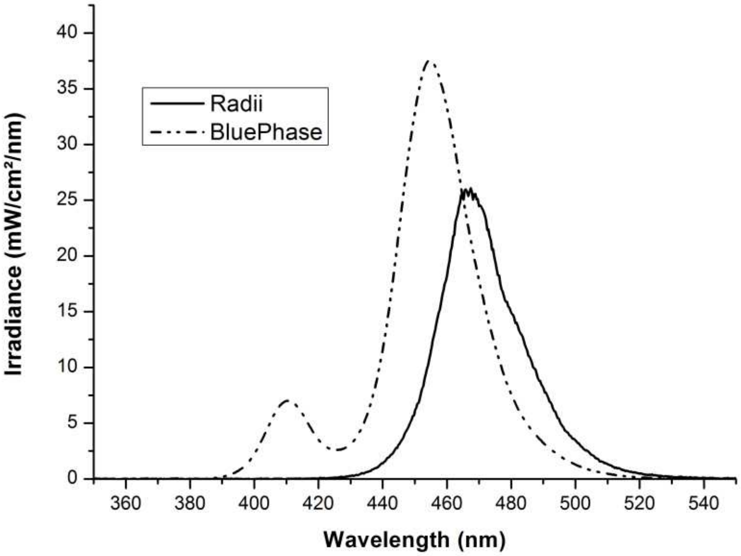

Figure 1. Light spectra distribution of the LCUs used in this study.

Curing kinetics

For the curing kinetics (CK), degree of conversion (DC) and maximum rate of polymerization (RPmax) in 5 minutes evaluation, 3µL of each adhesive tested was placed over the horizontal diamond element of an attenuated total reflectance (ATR) unit attachment (Golden Gate, Specac, Woodstock, GA, USA) in the optical bench of a Fourier transform infrared spectrometer (Tensor Series, Brucker Optik GmbH, Ettlingen, Germany). The photoactivation was conducted using a monowave (Radii-cal) or a polywave (Bluephase G2) LED, using a standardized energy dose of 48J/cm^2. The photoactivation distance was also standardized at 3mm from each adhesive drop, by using a Teflon separator, in which the LCU tip was positioned and conducted the photoactivation approach.

Thereafter, the infrared spectra were collected between 1680 and 1500 cm^{-1} at a rate of one spectrum per second (16 scans/spectrum) at 4 cm^{-1} resolution. Data were counted from the moment the infrared scan showed that the adhesive was stabilized on the ATR surface (to be the unpolymerized value) and the photoactivation was conducted continuously during each 1-second interval for 5 minutes. Seven replications (n=7) were made for each test condition based on previous studies using the same methodology (Arrais *et al.*, 2008; Arrais *et al.*, 2009). The degree of conversion was calculated using standard methods that evaluate changes in the ratios of aliphatic-to-aromatic C=C absorption peaks (1636 cm^{-1}/1608 cm^{-1}) in the uncured and cured states obtained from the infrared spectra. Before determining the monomer conversion, calibration graphs were made relating the absorbance ratios of known molar concentrations of aliphatic and aromatic C=C to their respective absorbance height ratios. Maximum DC in 5 minutes (DCmax), Rpmax and the kinetics distribution during the time of analysis were collected. For the statistical analysis, the data were analyzed by two-way ANOVA and Tukey's post-hoc test. Statistical significance was established at $\alpha = 0.05$.

Results

The DCmax and RPmax values are shown in the Table 1 and Table 2 respectively. Nevertheless, the maximum DC in 5 min values showed that the adhesives containing BAPO had a higher monomer conversion reaction ($p \leq 0.05$). For the Rpmax, the polywave LED Bluephase G2 showed better results for the BAPO containing adhesives when compared to the other groups ($p \leq 0.001$). Also, when the experimental resin blends were photocured with Radii-Cal, BAPO/amine and BAPO showed the highest RPmax values in comparison to the other adhesives. For the Bluephase G2 (Figure 2) and Radii-Cal (Figure 3), the curing kinetics showed that for BAPO and

BAPO/amine adhesives the curing reaction occurred faster and with higher DC values. On the other hand, the PPD group showed the lowest curing reaction.

Table 1. Means and standard deviation (SD) for the maximum degree of conversion in 5 minutes of the curing kinetics for the adhesives tested.

Adhesives	**Bluephase G2**	**Radii-Cal**
CQ/DMAEMA	44.74 (2.54) Bd	52.33 (1.16) Ac
PPD/DMAEMA	61.86 (3.69) Ac	67.47 (0.68) Ab
CQ/PPD/DMAEMA	39.07 (1.37) Be	48.53 (1.18) Ad
BAPO/DMAEMA	74.11 (1.55) Aa	71.21 (0.75) Aa
BAPO	73.86 (0.50) Aa	71.84 (0.75) Aa
CQ/BAPO/DMAEMA	67.19 (0.87) Ab	65.73 (0.45) Ab
PPD	9.51 (1.36) Af	11.06 (2.55) Ae
ADPER SCOTCHBOND	67.81 (0.27) Ab	67.66 (0.34) Ab

Different uppercase letters in the row and lowercase letters in the column means statistical significance (α=0.05).

Table 2. Means and standard deviations (SD) of the maximum rate of polymerization (conversion in %/s) in 5 minutes of the curing kinetics for the adhesives tested.

Adhesives	**Bluephase G2**	**Radii-Cal**
CQ/DMAEMA	3.13 (0.36) Ad	2.70 (0.50) Ac
PPD/DMAEMA	3.89 (0.45) Ad	3.47 (0.53) Ac
CQ/PPD/DMAEMA	2.66 (0.34) Ad	3.20 (0.61) Ac
BAPO/DMAEMA	28.02 (4.38) Aa	13.57 (1.48) Ba
BAPO	30.50 (1.25) Aa	14.23 (1.01) Ba
CQ/BAPO/DMAEMA	15.06 (2.48) Ab	3.99 (0.76) Bc
PPD	2.71 (0.51) Ad	2.67 (0.21) Ac
ADPER SCOTCHBOND	10.26 (0.65) Ac	8.29 (0.79) Ab

Different uppercase letters in the row and lowercase letters in the column means statistical significance (α=0.05).

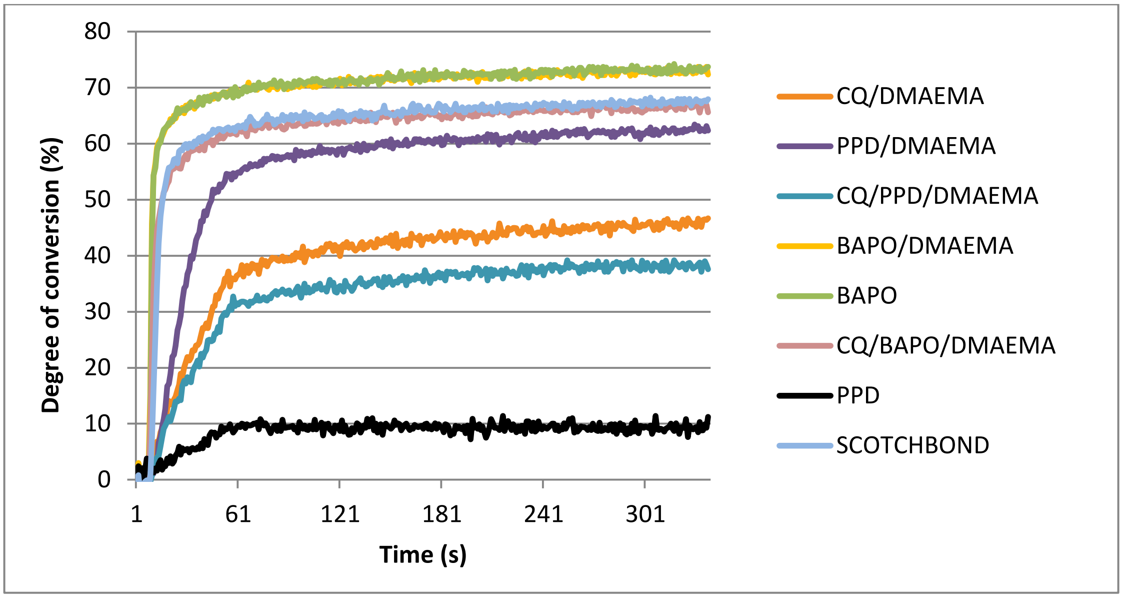

Figure 2. Curing kinetics behavior in 5 min for the groups tested photoactivated by Bluephase G2.

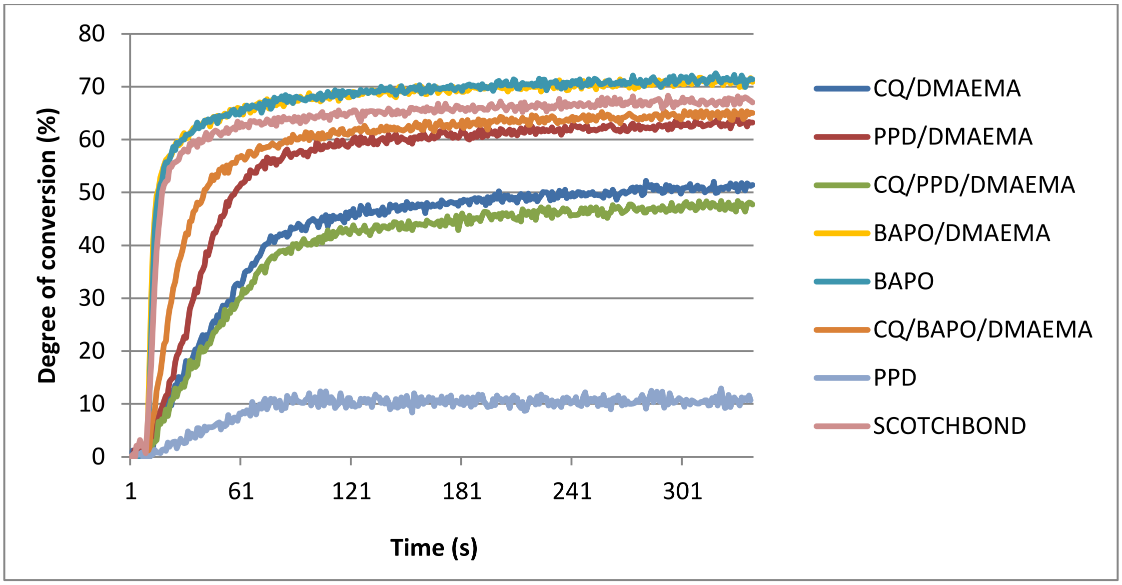

Figure 3. Curing kinetics behavior in 5 min for the groups tested photoactivated by Radii-Cal.

Discussion

In order to improve the optical and physical properties and overcome the shortcomings of dental composites formulated with the conventional CQ/amine system, alternative photo-initiators, such as PPD and BAPO have been used. The objective of replacing CQ by these formulations is to increase the color stability, enhance the curing performance and decrease the hydrolysis for the adhesive system, thus, reducing the necessity of replacing restorations. In this sense, this study evaluated the curing kinetics of hydrophobic resins from three-step etch-and-rinse adhesives, as well as the degree of conversion and rate of polymerization in 5 minutes of monitoring of cure.

The first hypothesis tested was partially accepted, since the experimental resins containing PPD/amine and BAPO showed similar or higher DC and RPmax values as the conventional photo-initiator systems, when real-time monitored for 5 minutes. When the CQ/amine adhesives were evaluated (experimental CQ/amine and the hydrophobic resin of Scotchbond Multi Purpose – control group) it was shown that the control group presented higher DC when compared to the experimental adhesive, probably because of the lower photo-initiator and co-initiator content of this adhesive (0.4 wt% of CQ and 0.4 wt% of DMAEMA), when compared to the comercial adhesive, in which MSDS does not state the photo-initiator system concentration. Many authors testing experimental BisGMA/HEMA resins use higher concentration of photo-initiators or co-initiators, showing higher DC when compared to the obtained in this study (Breschi *et al.*, 2009; Singh *et al.*, 2010).

Aditionally, the BAPO-containing adhesives present higher degree of conversion, regardless of the presence of the co-initiator content. For the current study, BAPO was tested with and without the addition of an amine as co-initiator, and it is clear that the addition of DMAEMA did not lead to significant chance in DC. This outcome confirms previous studies assuming that BAPO do not require a co-initiator for effective photopolymerization (Newmann *et al.*, 2006; Ikemura *et al.*, 2008). Following light absorption, BAPO is cleaved, generating reactive molecules capable of initiating the polymerization process (Newmann *et al.*, 2006; Ikemura *et al.*, 2010). CQ in contrast, is extremely dependent on the co-initiator, with direct effects on the physical properties of the material (Schneider *et al.*, 2008; Schneider *et al.*, 2012).

PPD have been studied as a promising substitute for CQ. In the present study, the PPD/amine adhesive, regardless of the LCU, showed a satisfactory DC when compared to the CQ/amine group or the control group. However, when used without the amine as a co-initiator, this adhesive formulation showed a poor monomer conversion, at a bout 9 to 10%. Conventionally, PPD is considered a Norrysh type I photo-initiator, which the polymerization reaction undergo a unimolecular bond cleavage upon light irradiation to yield free radicals (Albuquerque *et al.*, 2013; Brandt *et al.*, 2013). However, as shown in this study, for the neat hydrophobic resin using the organic matrix BisGMA/HEMA (60/40 wt%), the photo-cleavage expected by the PPD was not sufficient to guarantee an adequate DC different from some other studies (Sun and Chae, 2000; Shroeder *et al.*, 2007). Differently from BAPO, PPD photo-cleavage between the carbonyls reaction by itself does not promote a satisfactory carbon double bond conversion, needing the presence of a co-initiator to allow the formation of free radicals, such as the conventional CQ/amine systems. Some ketones undergo in both polymerization ways, and PPD is shown not only to work as a photo-initiator, but also as a photo-crosslinking agent, increasing the cross-link density of the polymer network, improving the physical-mechanical properties of the polymer (Brandt *et al.*, 2013).

The second hypothesis tested was partially rejected, since the monowave and polywave LEDs showed similar curing performance for the experimental adhesives, except for CQ/amine and CQ/PPD/amine. The alternative photo-initiators used in this study have the spectrum range varying from 310 to 500 nm, with the peak at about 397-400 nm. Even with a lower absorption peak compared to the LCUs used in this study, both LEDs showed an excelent curing performance, regardless of the photo-initiator content, probably due to the molar extinction coefficients which shows the absorption efficiency of these photo-initiators (Brandt *et al.*, 2013; Newmann *et al.*, 2006)

The formulation of adhesives containing BAPO and PPD should be encouraged, in order to evaluate the impact of these adhesives also in another types of systems, such as 2-step etch-and-rinse and the self-etch categories. Further studies analyzing another physical properties, such bond strength to enamel and dentin, marginal adaptation and permeability of the polymer network should be performed evaluate the inclusion of alternative photo-initiators in the adhesive composition.

Conclusion

In conclusion, the adhesives containing BAPO showed higher curing performance, showing a higher rate of polymerization and higher monomer conversion regardless of the LCU used. PPD alone did not have a satisfactory polymerization behavior, showing the dependence of the co-initiator to start and continue the polymerization reaction. The monowave LED had similar curing behavior when compared to the polywave one.

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Capítulo 2

Effect of PPD and BAPO on the physical-mechanical properties and marginal adaptation of dental adhesives

Abstract

The aim of this study was to evaluate the degree of conversion (DC), flexural strength (FS), flexural modulus (FM), yellowing (YL) and marginal adaptation (MA) of experimental adhesives containing alternative photoinitiators. Experimental hydrophobic adhesive resins containing BisGMA/HEMA as organic matrix were manipulated, with different photoinitiator content: G1- CQ/amine, G2- PPD/amine, G3- CQ/PPD/amine, G4- BAPO/Amine, G5- BAPO, G6- CQ/BAPO/Amine and G7- the hydrophobic resin of Adper Scotchbond Multi-Purpose as control. Bar-shaped specimens were made and photoactivated by a polywave (Bluephase G2) or a single-peak LED (Radii-cal), using 48J of energy dose. After 24hs, the DC was analyzed by FTIR and then the FS and FM were measured using the three-point bending test in a universal testing machine (0.5 mm/min). Disks speciments were made to evaluate the YL using a spectrophotometer. For the MA, composite restorations were made in human molars and then the superficial and internal margins were replicated and analyzed by SEM. DC, FS, FM and YL data were submitted to two-way ANOVA and Tukey's test at a preset alpha of 0.05. MA data was submitted to Kruskal-Wallis at a preset alpha of 0.05. The BAPO, BAPO/amine and the control adhesives showed higher DC, FS and FM values compared to the other resins. The YL was lower for the BAPO containing adhesives, followed by the PPD as photo-initiator. Also, BAPO alone guaranteed lower gap formation. In conclusion, CQ can be replaced by BAPO and PPD in hydrophobic adhesive resins, since it can enhance the physical properties and decrease YL and gap formation of these restorative materials.

Keywords: light curing unit, dental resin, polymerization.

Introduction

The 3-steps etch-and-rinse adhesives have been widely used in direct and indirect restorations. The three-step etch-and-rinse has been considered the clinical gold standard in dental bonding (Peumans *et al.*, 2005; De Munk *et al.*, 2005), especially due to the application of a hydrophobic resin coating. This neat resin layer is responsible for better *in vitro* and *in vivo* performance than the one-bottle etch-and-rinse adhesives (Armstrong *et al.*, 2003; Loguercio *et al.*, 2014). Usually light-cured, these adhesives are formulated with camphorquinone as the initiator combined to a tertiary amine as co-initiator (CQ/amine). However, CQ/amine has some drawbacks such as strong yellow coloration compromising aesthetic properties, low polymerization rate and efficiency, needing the presence of a amine co-initiator which could affect the biocompatibility and be oxidized over time (Nomura *et al.*, 2006; Cadenaro *et al.*, 2010; Schroeder & Vallo, 2007).

So, in order to overcome these problems, alternative photo-initiator systems such as phenyl-propanedione (PPD) and phenylbis(2,4,6-trimethylbenzoyl)phosphine oxide (BAPO) have been investigated (Brandt *et al.*, 2013; Albuquerque *et al.*, 2013). These agents are considered a Norrysh type I photo-initiator, in which the light irradiation promotes a bond cleavage reaction to yield free radicals (Albuquerque *et al.*, 2013; Brandt *et al.*, 2013). Thus, these photo-initiators theoretically do not require a co-initiator for effective photopolymerization (Newmann *et al.*, 2006; Ikemura *et al.*, 2008). CQ in contrast, is extremely dependent on the co-initiator, with direct effects on the physical properties of the material (Schneider *et al.*, 2008; Schneider *et al.*, 2012).

The light curing units (LCUs) should promote and adequate degree of conversion, guaranteed by either the satisfactory irradiance and the correct wavelength emitting unfiltered blues and/or violet light (Asmussen 2002; Faria-e-Silva *et al.*, 2010). The polywave LEDs are indicated by the manufacturers to cure these alternative photo-initiators, due to the additional LED emits light near to UV-Vis region (400 - 415 nm), even if the majority of LEDs in the dental market are monowave ones Some adhesive systems are not well cured with monowave LEDs (Asmussen 2002; Brandt *et al.*, 2010). The second peak in the UV-VIS region may promote a satisfactory cure of BAPO and PPD (Brandt *et al.*, 2010).

The aim of this study was to evaluate the effect of adhesives blends containing different photoinitiator systems in the degree of conversion (DC), flexural strength (FS), flexural modulus (FM), yellowing (YL) and marginal adaptation (MA), photoactivated by a monowave or a polywave LED. The first hypothesis tested is that alternative photoinitiators (PPD and BAPO) would have higher physical properties and marginal adaptation compared to the conventional CQ/AMINE system. The second hypothesis tested is that the polywave LED should provide a better curing performance and consequently increased properties for the adhesives containing the alternative photoinitiator systems.

Materials and methods

Resin Preparation

Six experimental hydrophobic adhesive formulations were tested in this study. The resin matrix for all adhesive formulations consisted of a combination of bisphenol glycidyl methacrylate – 60.0 wt% (BisGMA – Sigma-Aldrich Inc, St Louis, MO, USA); hydroxyethyl methacrylate – 40.0 wt% (HEMA - Sigma-Aldrich Inc, St Louis, MO, USA). The only difference among the adhesive blends was the photoinitiator system: camphorquinone (CQ), 1-phenyl-1,2-propanedione (PPD) or phenylbis(2,4,6-trimethylbenzoyl)phosphine oxide (BAPO). The photoinitiators were added to the matrix using the same molar concentration (1 mol%). The dimethylaminoethyl methacrylate (DMAEMA - Sigma-Aldrich Inc, St Louis, MO, USA) was used as co-initiators in the proportion 1:1 in some adhesive blends, as shown bellow: G1- CQ/DMAEMA; G2 – PPD/DMAEMA; G3- CQ/PPD/DMAEMA; G4 – BAPO/DMAEMA; G5 – BAPO; G6 – CQ/BAPO/DMAEMA; G7 – The hydrophobic resin from Adper Scotchbond Multi Purpose (used as control).

Light curing units (LCUs)

In the present study were used one monowave LED (Radii-Cal, 800 mW/cm^2, SDI, Victoria, Australia) and one polywave LED (Bluephase G2, 1200 mW/cm^2, Ivoclar Vivadent, Schaan, Liechtenstein). The output power (mW) of each LCU was measured using a calibrated power meter (Ophir Optronics, Har-Hotzvim, Jerusalém, Israel). Then, the irradiance (mW/cm^2) was calculated by dividing the output power by the tip area. The spectral distributions of the LCUs were obtained using a spectrometer (USB2000, Ocean Optics, Dunedin, FL, USA). These data (irradiance and spectral distribution) were integrated by using the Origin 6.0 software (OriginLab Northampton, MA, USA) as shown in Figure 1.

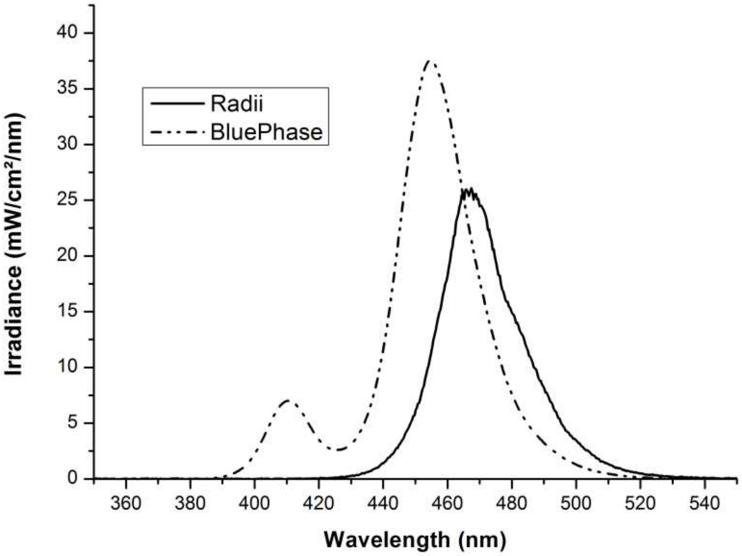

Figure 1. Light spectra distribution of the LCUs used in this study.

Degree of conversion

For the degree of conversion (DC) analysis, bar-shaped specimens (7 mm length x 2 mm width x 1 mm thickness) (n=7) were made in silicone molds and photo-activated by a monowave LED (Radii Cal, SDI, Victoria, Australia - 800 mW/cm^2 – 60s) or a polywave LED (Bluephase G2, Schaan, Liechtenstein – 1200mW/cm^2 – 40s) using an standardized energy dose of 48J/cm^2. After polymerization, the specimens were removed from the molds and stored dry in light-proof containers at 37ºC, for 24 hours. DC was measured on the top surface of each specimen using Fourier transformed infrared spectroscopy with attenuated total reflectance (FTIR/ATR - Spectrum 100, PerkinElmer, Shelton, CA, USA).

The absorption spectra of non-polymerized and polymerized composites were obtained from the region between 4000 and 650 cm−1 with 32 scans at 4 cm−1. The aliphatic carbon-carbon double-bond absorbance peak intensity (located at 1638 cm–1) and that of the aromatic (C…C) (located at 1608 cm–1; reference peak) were collected. The DC (%) was calculated using the following equation: DC (%) = 100 × [1 − (R polymerized/R non-polymerized)], where R represents the ratio between the absorbance peak at 1638 cm−1 and 1608 cm−1. The data were analyzed by two-way ANOVA and post hoc Tukey's test. Statistical significance was established at α=0.05.

Flexural strength and elastic modulus

Immediately after the DC analysis, the same bar-shaped specimens (n=8) were used for the three-point bending flexural test. The flexural test was performed according to ISO 4049, except for the specimen's dimensions (7 mm length x 2 mm width x 1 mm thickness). The three-point bending test was performed in a universal testing machine (Instron, Canton, USA – span between supports = 5 mm) at a cross-head speed of 0.5 mm/min. The maximum load for the specimens at fracture was recorded and the flexural strength (FS) calculated using the following equation: FS = 3FL/(2BH2), where F is the maximum load (N) exerted on the specimens; L the distance (mm) between the supports; B is the width (mm) of the specimens measured immediately prior testing; H is the height (mm) of the specimens measured immediately prior testing.

The elastic modulus was measured as the slope of the strain x strain curve in the linear portion, using the following equation: E = L1D310-3/4BH3D, where L1 is load (N);

D: distance (mm) between the supports; B: width (mm); H: height (mm); D: displacement (mm).

The data were analyzed by two-way ANOVA and post hoc Tukey's test. Statistical significance was established at α=0.05.

Yellowing effect

The experimental adhesives (n=5) were inserted in Teflon molds (6mm in diameter x 0,5mm thickness) with placement of a Mylar strip on the top and bottom surfaces. Then, the specimens were photoactivated for 40s using the polywave LED (Bluephase G2 – 1200mW/cm^2) and for 60s using the monowave LED (Radii Cal - 800 mW/cm^2), with and standardized energy dose of 48J/cm^2. Then, the specimens were stored dry in the dark for 24h at 37ºC. For the yellowing effect analysis, a spectrophotometer CM-700d (Minolta, Corp., Ramsey, NJ, USA) was utilized to measure the the b-axis parameter of the CIELab system. This parameter measures the yellow color of a material, with higher b-values relating to a greater yellowing effect. For the statistical analysis, the data were analyzed by two-way ANOVA and Tukey's post-hoc test. Statistical significance was established at α=0.05.

Marginal adaptation

Seventy healthy human third molars were selected. The teeth were collected after obtaining the patient's informed consent under a protocol approved by the ethical review board (#137/2011). The teeth were cleaned, included in polystyrene resin and their occlusal surfaces were polished with 320-grit SiC paper under constant water cooling (Politriz, AROTEC – São Paulo, SP, Brazil), to expose a flat dentin surface area. Then, typical Class I cavities were prepared using the standard preparation device (2mm deep), using #3131 diamond bur (KG Sorensen, Barueri, SP, Brazil) at a high-speed hand piece, under air/water-cooling. The bur was replaced after five preparations. After cavity preparation, teeth were randomly assigned to 14 groups (n=5) according to the two studied factors: adhesive system and light curing unit. All adhesives were photocured by using the LEDs tested.

All groups were restored with a microhybrid composite Z250 (A2 shade, 3M ESPE, St Paul, MN, USA). Then, the finishing and polishing procedures were performed with medium-, fine-, and extra fine- grit aluminum oxide disks (SoftLex – 3M ESPE, St Paul, MN, USA), after 24 h of water storage. After polishing, impressions of the teeth were taken, using a low viscosity vinyl polysiloxane material (Virtual, Ivoclar Vivadent, Schaan, Liechtenstein) and a first set of epoxy resin replicas (Epoxicure Resin, Buehler, Lake Bluff, IL, USA) was made for SEM evaluation and superficial marginal adaptation (SMA) evaluation.

Furthermore, each restoration was divided in the sagittal axis, new impressions of the teeth were taken and another set of replicas was made for each restoration for internal marginal adaptation (IMA) evaluation. All replicas were mounted on aluminum stubs, sputter coated with gold and were evaluated with a scanning electron microscope (JEOL, JSM-5600LV, Scanning Electron Microscope, Japan) as before at 200X magnification. SEM analysis of the composite/enamel marginal adaptation was performed by one operator having experience with quantitative margin examination and was blinded to the restorative procedures. The length of the gaps along the cavity margins was measured (mm) from the images using the UTHSCSA Image tool software version 2.0 developed by the Department of Dental Science at The University of Texas

Health Science Center (San Antonio, TX, USA). The marginal integrity between resin composite and enamel was expressed as a percentage of the entire superficial margin length. For the statistical analysis, as the data did not exhibit normal distribution (Kolmogorov-Smirnov test), a nonparametric test were carried-out (Kruskal-Wallis for groups' comparison) with a pre-set alpha of 0.05.

Results

The DC, FS, FM, YL, SMA and IMA values are shown in the Tables 1 to 6, respectively. After 24hs, the adhesives containing alternative photoinitiators and cured by the polywave LED showed higher DC when compared to the other adhesives ($p \leq 0.001$), except when PPD was associated to CQ and amine. BAPO/amine adhesive showed the higher DC mean among the groups tested. For the FS and FM, the adhesives containing BAPO showed the higher results when compared to CQ ($p \leq 0.001$). Only the control group presented similar results as the BAPO containing adhesives for FS and FM. In relation to the YL, the alternative photoinitiators showed less yellowing effect when compared to the adhesives containing CQ, and BAPO presented less YL values than PPD ($p \leq 0.001$). The LCUs promoted similar YL for the adhesives tested. Therefore, when analyzing the MA (superficial and internal), dentin sealing ability, the resin blends BAPO and BAPO/amine showed the low gap formation when compared to the other adhesives ($p \leq 0.001$).

Table 1. Means and standard deviation (SD) for the degree of conversion (%) for the groups tested.

Adhesives	Radii-Cal	Bluephase G2
CQ/DMAEMA	53.09 (3.31)Aab	58.29 (4.28)Ab
PPD/DMAEMA	53.34 (5.01)Bab	63.47 (3.62)Aab
CQ/PPD/DMAEMA	50.81 (5.88)Aab	48.57 (5.60)Ac
BAPO/DMAEMA	57.91 (3.58)Bab	69.90 (3.20)Aa
BAPO	51.89 (7.05)Bab	66.80 (3.76)Aab
CQ/BAPO/DMAEMA	49.89 (5.85)Bb	59.61 (4.88)Ab
ADPER SCOTCHBOND	60.34 (5.72)Aa	61.56 (2.04)Ab

Different uppercase letters in the row and lowercase letters in the column means statistical significance (α=0.05).

Table 2. Means and standard deviation (SD) for the flexural strength (Mpa) for the groups tested.

Adhesives	Radii-Cal	Bluephase G2
CQ/DMAEMA	118.16 (14.37) Ab	119.97 (16.67) Ab
PPD/DMAEMA	135.60 (29.72) Ab	115.50 (7.38) Ab
CQ/PPD/DMAEMA	77.50 (23.00) Ac	77.72 (23.70) Ac
BAPO/DMAEMA	184.62 (22.33) Aa	136.84 (17.35) Ba
BAPO	179.22 (22.62) Aa	146.35 (22.48) Ba
CQ/BAPO/DMAEMA	161.61 (14.85) Aa	141.92 (25.33) Aa
ADPER SCOTCHBOND	139.34 (28.80) Ab	138.60 (17.21) Aa

Different uppercase letters in the row and lowercase letters in the column means statistical significance (α=0.05).

Table 3. Means and standard deviation (SD) for the flexural modulus (Gpa) for the groups tested.

Adhesives	**Radii-Cal**	**Bluephase G2**
CQ/DMAEMA	1.52 (0.42) Ac	1.65 (0.36) Abc
PPD/DMAEMA	2.12 (0.30) Ab	1.27 (0.10) Bc
CQ/PPD/DMAEMA	0.90 (0.34) Ad	0.93 (0.32) Ac
BAPO/DMAEMA	2.72 (0.23) Aa	2.14 (0.20) Bab
BAPO	2.90 (0.14) Aa	1.96 (0.31) Ba
CQ/BAPO/DMAEMA	2.51 (0.18) Aab	2.14 (0.19) Aa
ADPER SCOTCHBOND	2.43 (0.59) Aab	1.87 (0.27) Bab

Different uppercase letters in the row and lowercase letters in the column means statistical significance (α=0.05).

Table 4. Means and standard deviation (SD) for the yellowing effect (b*) for the groups tested.

Adhesives	**Yellowing (b*)**	
	Radii-Cal	Bluephase G2
CQ/DMAEMA	8.2 (0.5) Ba	9.1 (0.6) Aa
PPD/DMAEMA	4.3 (0.2) Ac	4.3 (0.6) Ad
CQ/PPD/DMAEMA	2.3 (0.4) Bd	5.3 (0,3) Ac
BAPO/DMAEMA	4.1 (0.6) Bc	6.5 (0.3) Ab
BAPO	2.5 (0.8) Ad	3.2 (0.7) Ae
CQ/BAPO/DMAEMA	4.7 (0.6) Bc	6.4 (0.3) Ab
SCOTCHBOND MULTI PURPOSE	6.5 (1.2) Ab	6.4 (0.6) Ab

Different uppercase letters in the row and lowercase letters in the column means statistical significance (α=0.05).

Table 5. Means and standard deviation (SD) for the superficial marginal adaptation (%) for the groups tested.

Adhesives	Radii-Cal	Bluephase G2
CQ/DMAEMA	15.0 (26.7) B*	6.4 (10.7) B
PPD/DMAEMA	5.3 (9.7) B	19.5 (22.9) B*
CQ/PPD/DMAEMA	14.0 (25.2) B*	5.4 (10.0) B
BAPO/DMAEMA	14.6 (22.2) B	13.8 (25.6) B
BAPO	4.1 (10.5) B*	0.0 (0.0) A
CQ/BAPO/DMAEMA	5.8 (11.4) B	5.0 (9.3) B
SCOTCHBOND	1.6 (4.6) A	1.9 (5.3) AB

Different letters in the column and the presence of asterisks in the row means statistical significance (α=0.05).

Table 6. Means and standard deviation (SD) for the internal marginal adaptation (%) for the groups tested.

Adhesives	Radii-Cal	Bluephase G2
CQ/DMAEMA	6.1 (11.4) B	6.3 (15.2) B
PPD/DMAEMA	4.1 (9.7) B	2.0 (7.7) B
CQ/PPD/DMAEMA	9.5 (19.7) B*	1.0 (3.9) AB
BAPO/DMAEMA	2.1 (3.7) B*	0.0 (0.0) A
BAPO	0.0 (0.0) A	0.0 (0.0) A
CQ/BAPO/DMAEMA	8.2 (12.5) B*	3.5 (8.0) B
SCOTCHBOND	1.5 (4.1) AB	1.0 (3.9) AB

Different letters in the column and the presence of asterisks in the row means statistical significance (α=0.05).

Discussion

Alternative photo-initiators have been studied as an alternative to the conventional CQ/amine system, in an attempt to improve the optical and physical properties and overcome the drawbacks of the conventional photo-initiator systems of dental adhesives. Replace CQ by PPD and BAPO enhances the color stability and the physical properties and consequently the degradation of the polymer matrix (Albuquerque *et al.*, 2013; Brandt *et al.*, 2013). This is important to avoid replacing restorations and increasing the lifetime of the bonded interface. Thus, this study evaluated the physical-chemical properties and marginal adaptation of hydrophobic resins from three-step etch-and-rinse adhesives formulated with different photo-initiator systems cured with a polywave and a monowave LED.

The first hypothesis tested was partially validated, since most of the the tests performed in this study, the resins formulated with the alternative photo-initiators presented similar or better properties when compared to the conventional CQ/amine system. For the DC analysis, the resins containing BAPO and BAPO/DMAEMA showed higher curing potential than the other adhesive resins. This may be occured especially due to the fast photolysis of the carbono-phosphorus bond, generating benzoyl and phosphonyl radicals, which are both extremely reactive and capable of initiating vinyl monomer polymerization (Majima *et al.*, 1991; Medsker *et al.*, 1998). Due to the interaction of the carbonyl groups from BAPO with the central phosphonyl group higher amount of free radicals are produced, compared to the CQ/amine or PPD/amine systems (Rutsch *et al.*, 1996).

As a consequence, the higher in the DC should have improved the cohesive forces of the polymer network of these resins, which became more rigid to deformation and can ensure good clinical performance of these composites (Gonçalves *et al.*, 2010). So, the FS and FM were higher for the BAPO containing adhesives, when compared to the other groups. Although PPD is considered a cross-linking agent (Brandt *et al.*, 2013), the PPD containing adhesives did not showed high values of FM.

In relation to the YL effect, the experimental adhesives formulated with BAPO produced materials with lower yellowing than PPD/amine or CQ/amine. It probably occured due to the fact that BAPO exhibits a much higher molar extinction coeficient than PPD or CQ (Neumann *et al.*, 2005), producing a high DC and a better curing performance. This is explained by the higher molecule consumption during the photopolymerization reaction when compared to the conventional CQ/amine photo-initiator system. Also, the intrinsic color of BAPO is clearer than PPD and CQ, which may contributed to the lower YL values for the BAPO containing adhesives.

A satisfactory marginal seal of composite restorations is a primordial factor for its clinical success. The marginal adaptation have a crucial role in esthetics and bond durability. In the present work, specimens were not submitted to any mechanical or thermal stress and the composite restorative was standardized for all groups, in order to observe the gap formation related to the type of adhesive composition in relation to the photo-initiator content. However, it is important to state that besides the care taken during the sample preparation, gap formation studies usually shows high variability of the data. This is why a non- parametric statistical test was used in the presente study. Again, the adhesives containing BAPO showed less gap formation when compared to the other adhesives, probably due to the higher DC.

The second hypothesis was partially validated, since only for the DC analysis and YL of the experimental adhesives the monowave LED showed lower values when compared to the polywave Bluephase G2. For the DC, the polywave showed higher values when compared to the monowave, especially for the adhesives containing the alternative photoinitiators. It may happen because the polywave LED have an additional LED that emits light wavelengths near the UV-Vis Spectra (Brandt *et al.*, 2013) and it enhance the potential of cure for theses adhesives.

The formulation of adhesives containing BAPO and PPD should be encouraged, in order to evaluate the impact of these adhesives also in another types of systems, such as 2-step etch-and-rinse and the self-etch categories. Further studies analyzing another physical properties, such bond strength to enamel and dentin and permeability of the polymer network should be performed evaluate the inclusion of alternative photo-initiators in the adhesive composition.

Conclusion

Based on the results of the present study, the traditional CQ/amine photoinitiator system can be replaced by BAPO and PPD in formulations of hydrophobic adhesive resins, since it can enhance the physical properties and decrease YL and gap formation of these restorative materials. Also, the polywave LED curing unit, in general, induces a improved adhesive resins polymers due to the enhancement of the physical properties when compared to the monowave LED.

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Capítulo 3

Dentin permeability and sorption/solubility parameters of experimental dental adhesives containing alternative photo-initiators

Abstract

The aim of this study was to evaluate the water sorption (WS), water solubility (WSL) and dentin sealing ability (DSA) of experimental adhesives containing alternative photo-initiators photocured by LEDs. Experimental hydrophobic adhesive resins containing BisGMA/HEMA as organic matrix were manipulated, with different photoinitiator content: G1- CQ/amine, G2- PPD/amine, G3- CQ/PPD/amine, G4- BAPO/Amine, G5- BAPO, G6- CQ/BAPO/Amine and G7- the hydrophobic resin of Adper Scotchbond Multi-Purpose as control. For WS and WSL, adhesive disks (5x0.5mm, n=5) were prepared. After proper desiccation, the cured specimens were stored in distilled water for 7 days and then again desiccated, in order to measure the WS and WSL. The adhesives were cured with a polywave LED (Bluephase G2 - BF) or a monowave LED (Radii-Cal - RD), using 48J/cm^2 of energy dose. For DSA, middle-dentin disks were made and the maximum permeability was measured (10psi) after treatment with EDTA. Then, the adhesives were applied to the dentin, photoactivated and the DSA was re-measured. The DSA was expressed in terms of percentage of dentinal sealing. Data were submitted to two-way ANOVA and Tukey's test at a pre-set alpha of 0.05. All the experimental adhesives showed similar WS values, except for the BAPO/amine when cured with RD. For the WSL, the control group showed the lowest means when compared to the experimental adhesives. Moreover, for the DSA all the groups presented the same dentin permeability behavior, except by the BAPO/amine cured by

RD, showing a higher dentin sealing. In conclusion, CQ can be replaced by BAPO and PPD in hydrophobic adhesive resins, since it can show similar DS and WBS. However, the WS is increased when the adhesives were formulated using BAPO.

Keywords: light curing unit, dental resin, polymerization.

Introduction

Conventionally, the 3-steps etch-and-rinse adhesives have been widely used in direct and indirect restorations. Most of the adhesives are visible-light curable formulated with a binary photo-initiator system (camphorquinone as the initiator combined to a tertiary amine as co-initiator, CQ/amine). Therefore the popularity, this conventional photo-initiator system has some drawbacks such as strong yellow coloration compromising aesthetic properties (Albuquerque *et al.,* 2013), low polymerization rate and efficiency, needing the presence of a amine co-initiator which could affect the biocompatibility and be oxidized over time (Cadenaro *et al.*, 2010; Schroeder & Vallo, 2007).

So, in order to overcome these shortcomings, alternative photo-initiator systems such as phenyl-propanedione (PPD) and phenylbis(2,4,6-trimethylbenzoyl)phosphine oxide (BAPO) have been investigated (Brandt *et al.*, 2013; Albuquerque *et al.*, 2013). Nevertheless, these photo-initiators do not need an amine as co-initiator, been classified as Norrish Type-I molecules, which starts the polymerization process by direct cleavage (Brackett *et al.*, 2007).

Since the optical properties are one of the main reason for using the alternative photo-initiator systems, few studies exist showing some permeability properties, from the substrate and from the polymer, such as water sorption, water solubility and dentin sealing ability of dental adhesives formulated with such materials. In this sense, the quality of the association dentine/adhesive layer should prevent the long-term durability of the resin composite restoration. Even with the application of the solvent-free layer (hydrophobic resin coat) placed over the primed dentin, the polymer network degrades over time becoming a permeable membrane which could result in a worse sealing of the dentin surface (De Munk *et al.*, 2005; Cadenaro *et al.*, 2009).

Some adhesive systems are not well cured with monowave LEDs due to alternative photo-initiators content, which are excited by the light near to the UV-region of the spectra (Faria-e-Silva *et al.*, 2010). To overcome this problem, polywave third generation LEDs were introduced, emitting light wavelengths targeting the absorption peak of camphorquinone and an additional light output at the UV-Vis region of the electromagnetic spectrum (400 - 415 nm) (Price *et al.*, 2010; Brandt *et al.*, 2010). The second peak in the UV-VIS region may promote a satisfactory cure of these adhesives, containing alternative photo-initiators systems, since adequate LCU is primordial to yielding an adequate adhesive polymerization and resin physical properties.

The aim of this study was to evaluate the effect of adhesives blends containing different photo-initiator systems in the water sorption (WS), water solubility (WSL) and dentin sealing ability (DSA), photoactivated by a monowave or a polywave LED. The hypothesis tested is that alternative photo-initiators, such as PPD and BAPO, would have lower WS, WSL and higher DSA than the conventional CQ/AMINE system regardless of the light curing unit tested.

Materials and methods

Resin Preparation

Six experimental hydrophobic adhesive formulations were tested in this study. The resin matrix for all adhesive formulations consisted of a combination of bisphenol glycidyl methacrylate – 60.0 wt% (BisGMA – Sigma-Aldrich Inc, St Louis, MO, USA); hydroxyethyl methacrylate – 40.0 wt% (HEMA - Sigma-Aldrich Inc, St Louis, MO, USA). The only difference among the adhesive blends was the photo-initiator system: camphorquinone (CQ), 1-phenyl-1,2-propanedione (PPD) or phenylbis(2,4,6-trimethylbenzoyl)phosphine oxide (BAPO). The photo-initiators were added to the matrix using the same molar concentration (1 mol%). The dimethylaminoethyl methacrylate (DMAEMA - Sigma-Aldrich Inc, St Louis, MO, USA) was used as co-initiators in the proportion 1:1 in some adhesive blends, as shown bellow: G1- CQ/DMAEMA; G2 – PPD/DMAEMA; G3- CQ/PPD/DMAEMA; G4 – BAPO/DMAEMA; G5 – BAPO; G6 – CQ/BAPO/DMAEMA; G7 – The hydrophobic resin from Adper Scotchbond Multi Purpose (3M ESPE, St paul, MN, USA) (used as control).

Light curing units (LCUs)

The present study used one monowave LED (Radii-Cal, 800 mW/cm^2, SDI, Victoria, Australia) and one polywave LED (Bluephase G2, 1200 mW/cm^2, Ivoclar Vivadent, Schaan, Liechtenstein). The output power (mW) of each LCU was measured using a calibrated power meter (Ophir Optronics, Har-Hotzvim, Jerusalém, Israel). Then, the irradiance (mW/cm^2) was calculated by dividing the output power by the tip area. The spectral distributions of the LCUs were obtained using a spectrometer (USB2000, Ocean Optics, Dunedin, FL, USA). These data (irradiance and spectral distribution) were integrated by using the Origin 6.0 software (OriginLab Northampton, MA, USA) as shown in figure 1.

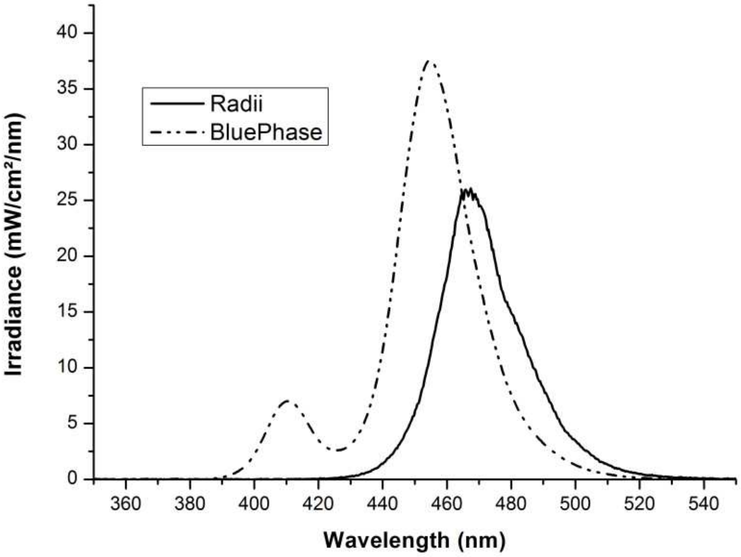

Figure 1. Light spectra distribution of the LCUs used in this study.

Dentin Sealing ability measurement

Seventy sound human molars of similar size were selected (n=5). This study had the approval of the Ethical Committee of the Institutional Review Board. Middle dentin disks (0.9 mm thick) were obtained at 2mm up to the cementoenamel junction by using a diamond saw (Isomet 1000, Buehler Ltd, Lake Bluff, IL, USA) at 300 rpm. The dentin thickness was measured by using a caliper (Golgran, São Paulo, SP, Brazil). The exposed middle dentin was further polished on wet #600-grit silicon-carbide paper for 60s to standardize the smear layer.

For the dentin sealing ability measurement, the disk was attached to a device platform that was perforated in the center and connected to a hydraulic pressure device that delivered 10 psi (703 cm H_2O or 51.7 cm Hg) of water pressure during the measurement of the dentin permeability (Pashley & Depew 1986; Sauro *et al.*, 2007, Sá *et al.*, 2012).

Next, three permeability measurements were taken using a permeability device (THD – O2b, Odeme, Joaçaba, SC, Brazil). First of all, an initial permeability was taken in order to measure to the disks without any treatment, just to aleatory rearrange the groups. Thereafter, for the maximum fluid filtration (MFF), the dentin disk was immersed in 0.5 M EDTA (pH 7.5) for 5 minutes, with further water rinsing for 1 minute and ultrasonic cleaning (Maxi Clean 750, Unique, Indaiatuba, SP, Brazil) in water for 5 minutes. This initial measurement was defined as 100% dentin permeability. After measuring the MFF (µl/min), a new smear layer was created on the dentin surface, by using again the wet #600-grit silicon-carbide paper for 60s. The dentin surface was acid etched with conventional phosphoric acid (Condac 37, FGM, Joinville, PR, Brazil) with posterior rising and drying, leaving the dentin gently moist. Then, the primer solution (Scotchbond Multi Purpose, 3M, ESPE, St Paul, MN, USA) was applied actively to the dentin for 20s, with posterior solvent air-drying for 10s; the experimental adhesives and the control were applied to the respective specimens and then photoactivated by using a monowave LED (Radii-cal, 60s) or a polywave LED (Bluephase G2, 40s). No resin composite was applied over the bonding agents, due to a direct exposure of adhesives to water. Then, after 2 hours of bonding, the fluid flow through hybridized dentin (FFHD) was measured to calculate the percentage of dentin permeability reduction (dentin sealing) provided by the adhesives. The dentin sealing was calculated using the following formula: Dentin sealing (%) = 100 x (MFF – FFHD)/MFF.

Water Sorption and Solubility

This study was performed in compliance with ISO 4049:2000 standard specifications (except for the specimen dimensions and curing protocol) as follows. To verify the sorption (WS) and solubility (WBS), circular samples (0.5 mm thickness x 6 mm diameter) (n=5) were photo-activated by the LEDs (Radii-Cal, SDI, Victoria, Australia - 800 mW/cm^2 or Bluephase G2, Ivoclar Vivadent, Schaan, Liechtenstein – 1200 mW/cm^2) using a standard energy dose of 48J/cm^2. The specimens were stored in desiccators containing silica gel at 37ºC and weighed daily using an analytical balance (Tel Marke, Bel Quimis, São Paulo, SP, Brazil) accurate to 0.0001 g, until a constant mass (m1) was obtained (i.e. three days of no weight change). Thickness (four measurements at four equidistant points on the circumference) and diameter of each specimen were measured using a digital electronic caliper (Mitutoyo Corporation, Tokyo, Japan). Mean values were used to calculate the volume (V) of each specimen (mm^3). Thereafter, the samples were stored in plastic containers with 6 mL of distilled water at 37ºC for 7 days and weighed daily after carefully wiping with absorbent paper. When constant weight was obtained (two days of no weight change), this value was recorded as m2, and the samples were returned to the desiccators. The entire mass reconditioning cycle was repeated and the constant mass (two days of no weight change) was recorded as m3. The values for water sorption (WS) and solubility (WSB), in micrograms per cubic millimeters, were calculated using the following equations:

$$WS = (m2 - m3) / V$$

$$WSB = (m1 - m3) / V$$

Statistical analyses

The data were analyzed by two-way ANOVA and Tukey's post-hoc test.

Statistical significance was established at α=0.05 for all tests.

Results

The water sorption (WS), water solubility (WSL) and dentin sealing ability (DSA) values are shown in the Tables 1, 2 and 3 respectively. For the water sorption, when the adhesives were photoactivated by the polywave LED, there was no significant difference among the groups ($p \geq 0.05$). However, when cured using Radii-Cal LED, the adhesive BAPO/DMAEMA showed the higher values. The water solubility showed that in general, the adhesives containing BAPO showed lower solubility when compared to the other groups ($p \leq 0.001$). Also, the third generation LED promoted higher water sorption to the specimens when compared to the second generation one. Therefore, when analyzing the dentin sealing ability, the resin blends CQ/amine and PPD/amine showed the worst means, regardless of the LCU used. Also, BAPO/amine adhesive decreased the dentin permeability ($p \leq 0.001$), as shown in the Table 3.

Table 1. Means and standard deviation (SD) for the water sorption of the groups tested.

Adhesives	**Water sorption**	
	Bluephase G2	Radii-Cal
CQ/DMAEMA	89.8 (7.1) Aa	77.8 (15.0) Bb
PPD/DMAEMA	87.1 (13.4) Aa	67.9 (8.0) Bb
CQ/PPD/DMAEMA	93.7 (7.9) Aa	62.28 (8.0) Bb
BAPO/DMAEMA	94.9 (10.2) Aa	90.5 (5.9) Ba
BAPO	92.3 (14.9) Aa	83.5 (9.2) Bb
CQ/BAPO/DMAEMA	90.9 (9.5) Aa	86.3 (9.2) Bb
SCOTCHBOND MULTI USO	84.0 (15.7) Aa	75.0 (9.4) Bb

Different uppercase letters in the row and lowercase letters in the column means statistical significance (α=0.05).

Table 2. Means and standard deviation (SD) for the water solubility of the groups tested.

Adhesives	**Water solubility**	
	Bluephase G2	Radii-Cal
CQ/DMAEMA	60.3 (8.3) Ba	76.4 (11.6) Aa
PPD/DMAEMA	21.4 (10.9) Bb	33.9 (5.9) Ab
CQ/PPD/DMAEMA	68.4 (9.0) Ba	80.6 (8.0) Aa
BAPO/DMAEMA	70.3 (8.7) Aa	19.8 (5.9) Bc
BAPO	18.2 (10.6) Ab	19.8 (9.2) Ac
CQ/BAPO/DMAEMA	8.6 (9.3) Bb	46.7 (17.0) Ab
SCOTCHBOND MULTI USO	18.8 (10.3) Ab	0.0 (0.0) Bd

Different uppercase letters in the row and lowercase letters in the column means statistical significance (α=0.05).

Table 3. Means and standard deviation (SD) for the dentin sealing ability (%) of the groups tested.

Adhesives	Dentin Sealing ability (%)	
	Bluephase G2	Radii-Cal
CQ/DMAEMA	78.2 (15.4) Ab	78.10 (16.8) Ab
PPD/DMAEMA	73.9 (20.1) Ab	85.3 (3.9) Aab
CQ/PPD/DMAEMA	88.4 (5.3) Aab	82.1 (19.4) Aab
BAPO/DMAEMA	95.8 (2.3) Aa	93.2 (4.3) Aa
BAPO	88.6 (2.0) Aab	90.6 (5.8) Aab
CQ/BAPO/DMAEMA	88.1 (6.1) Aab	88.3 (6.2) Aab
SCOTCHBOND MULTI PURPOSE	91.0 (3.5) Aab	93.4 (5.9) Aa

Different uppercase letters in the row and lowercase letters in the column means statistical significance (α=0.05).

Discussion

Trying to enhance the physical-chemical properties and the resistance to degradation by hydrolysis and, the conventional CQ/amine photoinitiator system is being replaced or working together with alternative photoinitiator systems. So, the present study evaluated the effect of formulating hydrophobic resins from 3-step etch-and-rinse adhesives containing PPD or BAPO alone or in association to CQ and amine in the WS, WSL and DSA of theses adhesives.

The first hypothesis tested was not accepted, since the adhesive blends containing PPD and BAPO, alone or in association to CQ and amine showed similar WS, WSL and DSA to the conventional CQ/amine systems. This possible can be explained due to the similar potential of the LCUs in curing the experimental adhesives. Even if BAPO and PPD having the most important absorption peaks between 400 and 440 nm, their molar extinction coefficient is higher than the CQ/amine system (Neumann *et al.*, 2006; Brandt *et al.*, 2013), which could have contributed to the similar WS results using each LCU.

The WS is an important property, which can predict the permeability of the polymer network. The water penetration leads to a relaxation process on the macromolecular polymer chains, causing a polymer softening by swelling the polymer network and reducing the frictional forces between the polymer chains (Ferracane *et al.*, 1998). Also, for the WSL, the BAPO alone containing adhesives as well as the commercial adhesive (control group) showed lower values compared to the other resin blends. This may have happened due to the higher rate of polymerization presented by these adhesives, in which polymer network could have formed more cross-link density (Brandt *et al.*, 2013). The unreacted monomers trapped in the polymer network are released by water at a rate that is controlled by the swelling and relaxation capacities of the polymer (Malacarne *et al.*, 2006) and the increase in the permeability will facilitate fluid transport in and out of the network, leading to enhanced water uptake and elution (Schneider *et al.*, 2009).

In relation to the DSA, there were differences between the BAPO/amine and CQ/amine blends, where the alternative photo-initiator system showed higher dentin sealing. The other groups showed similar values of dentin permeability. All of them showed satisfactory DSA means, probably due to the fact that the 3-step etch-and-rinse adhesive systems are the gold standard among the categories of bonding agents (De Munk *et al.*, 2005; Breschi *et al.*, 2008). Further, it is known that the dentin sealing ability used hydraulic pressure, which is directly related to the permeability of the adhesive layer in the dentinal tubules and all adhesives presented similar WS values. In accordance to the present study, Sá *et al.* (2012) stated that the 3-step etch-and-rinse adhesive Adper Scotchbond Multi Purpose showed similar immediate results for DSA.

In the present study, BAPO was tested with and without the addition of an amine as co-initiator, and it is clear that the addition of DMAEMA did not lead to an increase of the dentin sealing and WS and WSL properties. This outcome confirms previous studies suggesting that BAPO do not require the amine as a co-initiator for effective photoactivation (Newmann *et al.*, 2005). When light reaches the BAPO molecule, it is cleaved, generating reactive molecules capable of initiating the polymerization process (Newman *et al.*, 2005). The conventional CQ photo-initiator in contrast, is extremely dependent on the tertiary amine content, with direct effects on the mechanical and optical properties of the material (Albuquerque *et al.*, 2013; Brandt *et al.*, 2013).

The formulation of adhesives containing BAPO and PPD should be encouraged, in order to evaluate the impact of these adhesives also in another types of systems, such as 2-step etch-and-rinse and the self-etch categories. Further studies analyzing another physical properties, such as the curing performance, bond strength, marginal adaptation should be performed, evaluating the inclusion of alternative photo-initiators in the adhesive composition.

Conclusion

Based on the results of the present study, the adhesives containing the alternative photoinitiators showed similar dentin sealing ability and lower water solubility as the conventional CQ/amine or PPD/amine adhesives. However it also induced higher water sorption specially the blend formulated with the alternative photoinitiator system BAPO/amine cured with RD. The BF showed lower solubility and higher water sorption when compared to RD.

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CAPÍTULO 4

Long-term dentin bond durability of experimental three-step dental adhesives containing phenylpropanedione and bisalquylphosphine oxide

Abstract

The aim of this study was to evaluate the immediate and 1-year water storage microtensile bond strength (µTBS) and the failure modes of experimental adhesives containing alternative photo-initiators photocured by LEDs. Experimental hydrophobic adhesive resins containing BisGMA/HEMA as organic matrix were manipulated, with different photoinitiator content: G1- CQ/amine, G2- PPD/amine, G3- CQ/PPD/amine, G4- BAPO/Amine, G5- BAPO, G6- CQ/BAPO/Amine, G7- the hydrophobic resin of Adper Scotchbond Multi-Purpose as control. Seventy human molars were selected and exposed the middle dentin. Then, adhesives were applied and photocured using a polywave (Bluephase G2) or a monowave (Radii-Cal) LED, with standardized energy dose of 48J. The specimens were restored using a microhybrid composite and longitudinally sectioned to obtain bonded sticks (0.9 mm^2) to be tested in tension at 1 mm/min until failure. Half of the sticks were tested after 24hs and the other half after 1-year of water storage. The failure mode then was recorded. The µTBS data were submitted to two-way repeated measures ANOVA and Tukey's test (α=0.05). At the immediate evaluation, regardless of the light curing unit (LCU) used, the BAPO/amine adhesives showed the highest µTBS values compared to the other groups. The polywave LED promoted higher µTBS results compared to the monowave LED for the BAPO alone adhesive after 24hs. Moreover, after 1-year of water storage, all µTBS means decreased, except the BAPO-containing adhesives showed higher results. In conclusion, the alternative photoinitiator BAPO can replace CQ in three-step dental adhesives, since it shows higher µTBS immediately and after 1-year of water storage. The LCU influenced the µTBS results for the experimental adhesives.

Keywords: photoactivation, light curing units, photo-initiators.

Introduction

One concern regarding the adhesive restorations is their limited durability, which can cause retention loss, as well as the gap formation and marginal discoloration (Peumans *et al.*, 2005; Heintze *et al.*, 2010). They are the main factors that yield to the restoration replacement. In this sense, the three-step etch-and-rinse adhesives have been widely used in composite restorations and has been considered the clinical gold standard in dental bonding (Peumans *et al.*, 2005; De Munk *et al.*, 2005), especially due to the application of a hydrophobic resin coating. This neat resin layer is responsible for better *in vitro* and *in vivo* performance than the one-bottle etch-and-rinse adhesives (Armstrong *et al.*, 2003; Albuquerque *et al.,* 2013).

It is well known that hybrid layer is a mixture of dentin organic matrix, residual hydroxyapatite, resin monomers and solvents (Nakabayashi *et al.*, 1992). For a stable resin-bonded interface the monomer impregnation and conversion into the mineralized/demineralized dentin substrate is needed. The monomer conversion of three-step etch-and-rinse adhesives usually depends on the photo-initiator system, which is usually the conventional binary CQ/amine (camphorquinone as the initiator combined to a tertiary amine as co-initiator). Although it has been used for too long time in dentistry, this conventional photo-initiator system has some drawbacks such as the yellowing effect due to its intrinsic coloration, low polymerization rate and efficiency with the need of an amine co-initiator, and cytotoxicity and genotoxicity (Cadenaro *et al.*, 2010; Schroeder & Vallo, 2007; Nomura *et al.*, 2006).

So, in order to overcome these shortcomings, alternative photo-initiator systems (such as phenyl-propanedione (PPD) and bisalquyl phosphine oxide (BAPO) have been studied (Brandt *et al.*, 2013; Albuquerque *et al.*, 2013). In addition, these photo-initiators do not need an amine as co-initiator, been classified as Norrish Type-I molecules, which starts the polymerization process by direct cleavage (Brackett *et al.*, 2007).

Also, for a satisfactory conversion, the light curing unit (LCU) should emitt a satisfactory irradiance, as well as the correct wavelength according to the photo-initiator used (Asmussen *et al.*, 2002). The LCU should guarantee a satisfactory curing performance of the adhesive and the light emitting diodes (LEDs) have been shown to effectively cure dental adhesives, emitting unfiltered blues and/or violet light (Asmussen 2002; Faria-e-Silva *et al.*, 2010). Since some commercial adhesives are formulated using alternative photo-initiators, such as phenyl propanedione (PPD), bis-alquyl phosphinic oxide (BAPO) (Brandt *et al.*, 2010), the third generation polywave LEDS were introduced (Brandt *et al.*, 2010; Price *et al.*, 2010) in order to deliver additional light output at the UV-Vis region of the electromagnetic spectrum (400 - 415 nm). The second peak in the UV-VIS region may promote a satisfactory cure of the alternative photo-initiators.

There is no study concerning the bond strength durability using adhesives containing PPD or BAPO as photo-initiators. Thus, the aim of this study was to evaluate the effect of dentin microtensile bond strength (µTBS) immediately and after 1-year in water degradation of adhesives blends containing different photoinitiator systems. The first hypothesis tested was that alternative photoinitiators (PPD and BAPO) would promote higher bond strength values than the conventional CQ/AMINE system. The second hypothesis tested is that the polywave LED should provide a better bond performance for the adhesives containing the alternative photoinitiator systems

Materials and methods

LED Curing Units

Two light-emitting diodes (LEDs) were tested: a polywave LED (Bluephase G2-BF, Schaan, Liechtenstein, 1200mw/cm^2) and a monowave LED (Radii-Cal – RD, SDI Limited, Victoria, Australia). Irradiance (mW/cm^2) was measured dividing the output power (measured by a calibrated power meter - Ophir Optronics, Har – Hotzvim, Jerusalem, Israel) by the tip end area of the LCUs. The Spectra of the LED units was measured with a calibrated spectrometer (USB2000, Ocean Optics, Dunedin, FL, USA), as shown in Figure 1. The energy dose was standardized to 48J J/cm^2 for the bonding systems curing approach.

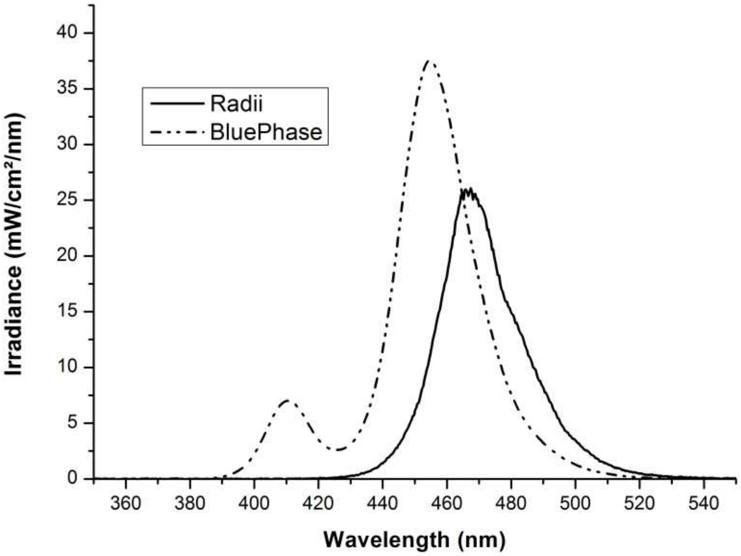


Figure 1. Light spectra distribution of the LCUs used in this study.

Resin Preparation

Six experimental hydrophobic adhesive formulations were tested in this study. The resin matrix for all adhesive formulations consisted of a combination of bisphenol glycidyl methacrylate – 60.0 wt% (BisGMA – Sigma-Aldrich Inc, St Louis, MO, USA); hydroxyethyl methacrylate – 40.0 wt% (HEMA - Sigma-Aldrich Inc, St Louis, MO, USA). The only difference among the adhesive blends was the photoinitiator system: camphorquinone (CQ), 1-phenyl-1,2-propanedione (PPD) or phenylbis(2,4,6-trimethylbenzoyl)phosphine oxide (BAPO). The photoinitiators were added to the matrix using the same molar concentration (1 mol%). The dimethylaminoethyl methacrylate (DMAEMA - Sigma-Aldrich Inc, St Louis, MO, USA) was used as co-initiators in the proportion 1:1 in some adhesive blends, as shown bellow: G1- CQ/DMAEMA; G2 – PPD/DMAEMA; G3- CQ/PPD/DMAEMA; G4 – BAPO/DMAEMA; G5 – BAPO; G6 –

CQ/BAPO/DMAEMA; G7– The hydrophobic resin from Adper Scotchbond Multi Purpose (used as control) (3M ESPE, St Paul, MN, USA).

Specimen's Preparation

Seventy sound human molars were selected (n=5). This study had the approval of the Institutional Ethical Committee Review Board. The teeth were cleaned, their roots inserted in polystyrene resin and the occlusal surfaces wet polished with 180-grit SiC paper under running water (Politriz, AROTEC – São Paulo, SP) in order to expose a flat dentin surface. The exposed middle dentin was further polished on wet #600-grit silicon-carbide paper for 60s to standardize the smear layer.

For the restorative procedure, the dentin surface was acid etched with conventional phosphoric acid (Condac 37, FGM, Joinville, SC, Brazil) with posterior rising and drying, leaving the dentin gently moist. Then, the primer solution (Scotchbond Multi Purpose, 3M, ESPE, St Paul, MN, USA) was applied actively to the dentin for 20s, with posterior solvent air-drying for 10s. Then, the experimental adhesives and the control one were applied to the respective specimens and then photoactivated by using a monowave LED (Radii-cal, 60s) or a polywave LED (Bluephase G2, 40s). Resin composite buildups (Filtek Z250 A2-shade, 3M ESPE, St Paul, MN, USA) were placed on the bonded surfaces (three increments of 1.5 mm each), wich were individually photoactivated by 20s.

Microtensile Bond Strength

After storage in distilled water at 37ºC for 24h, specimens assigned to the MTBS test were longitudinally sectioned in both "x" and "y" directions across the bonded interface using a diamond saw (Isomet 1000, Buehler Ltd, Lake Bluff, IL, USA) at 300 rpm to obtain sticks with a cross-sectional area of approximately 0.9 mm^2. The cross-sectional area of each stick thus was measured with the digital caliper to the nearest 0.01 mm and recorded for the bond strength calculation. The bonded sticks originated from the same teeth were assigned to testing immediately or after one year of storage in distilled water at 37ºC. The storage solution was replaced monthly.. Sticks were individually attached to a jig for microtensile testing with cyanoacrylate resin (Super Bond gel, Loctite, Henkel, Brazil) and subjected to a tensile force in a universal testing machine (EZ-TEST, Shimadzu, Japan) at a crosshead speed of 1.0 mm/min until failure.

Bond failure modes were evaluated with a scanning electron microscope (JEOL, JSM-5600LV, Scanning Electron Microscope, Japan) and classified as: 1) cohesive (failure exclusive within dentin or resin composite, 2) adhesive (failure at resin/dentin interface or cohesive in adhesive resin) or 3) mixed (mixed with cohesive failure of the neighboring substrates). The obtained data were subjected to a two-way repeated measures ANOVA and Tukey´s test at a pre-set alpha of 0.05.

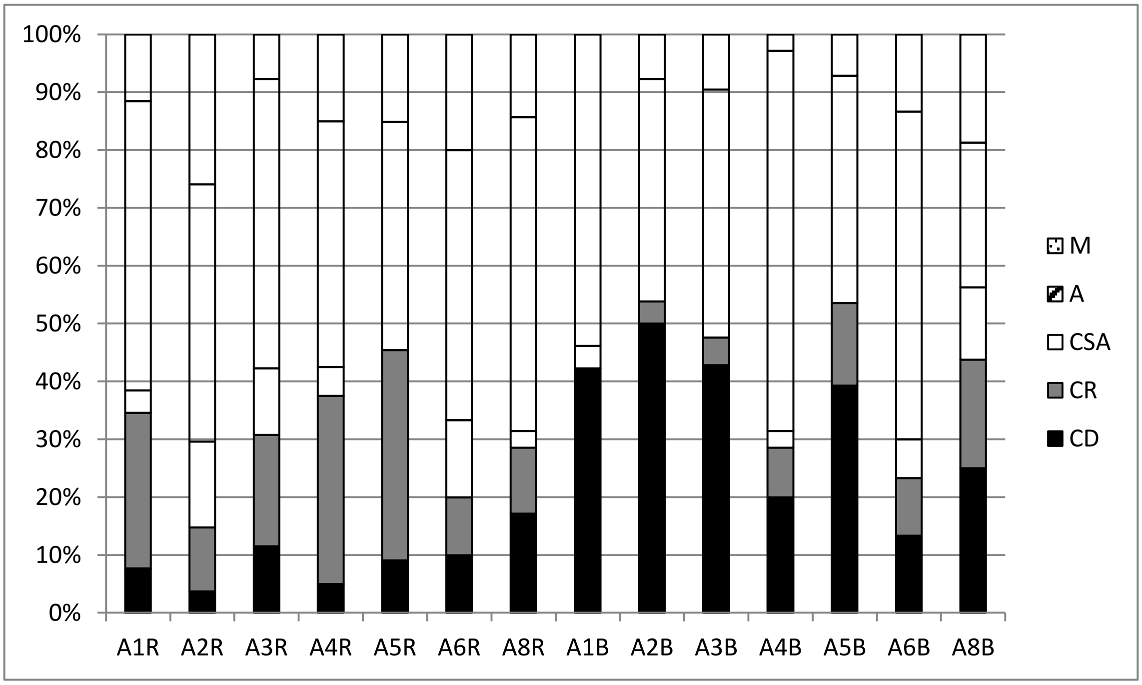
Results

The immediate and 1-year µTBS values for the groups tested are shown in the Table 1 and 2 respectively. For the bond failure analysis in each evaluated time (immediate and 1-year) graphs are showing the type and frequency of the failure modes (Figure 2 and 3). At the immediate analysis, the adhesives containing BAPO showed increased µTBS values when compared to the other adhesives tested ($p \leq 0.001$). Also, after 1-year of water storage, all values were decreased by water degradation, however the BAPO and BAPO/amine adhesives showed better results.

Table 1. Means and standard deviation for the immediate microtensile bond strength values for the groups tested.

Adhesives	**Immediate Bond Strength (Mpa)**	
	Bluephase G2	Radii Cal
CQ/DMAEMA	62.1 (5.4) Ab	67.2 (3.4) Aa
PPD/DMAEMA	40.5 (9.8) Ac	39.3 (8.6) Ab
CQ/PPD/DMAEMA	33.6 (4.6) Ad	46.3 (7.9) Ab
BAPO/DMAEMA	62.9 (4.0) Ab	64.6 (7.9) Aa
BAPO	80.2 (1.7) Aa	66.7 (7.6) Ba
CQ/BAPO/DMAEMA	57.1 (5.8) Ab	49.1 (10.7) Bb
SCOTCHBOND MULTI PURPOSE	58.6 (2.7) Ab	63.7 (2.2) Aa

Different uppercase letters in the row and lowercase letters in the column means statistical significance (α=0.05).



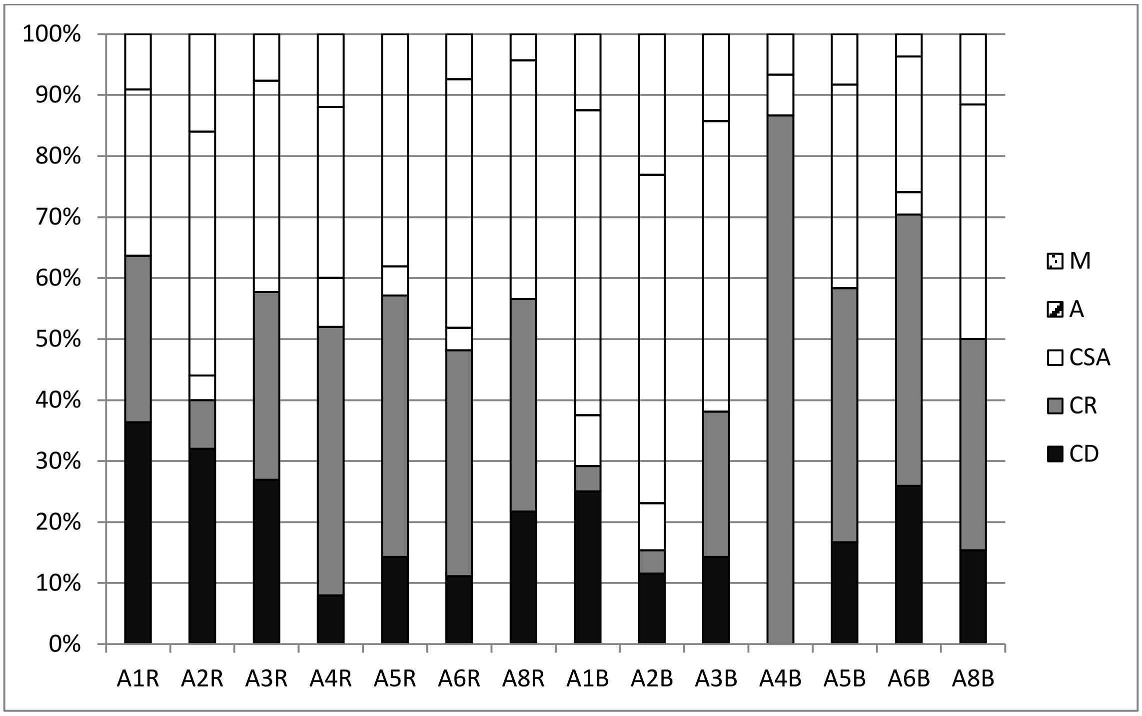
M – mixed failure; A – adhesive failure; CSA – cohesive failure in the adhesive layer; CR – resin cohesive failure; CD – dentin cohesive failure. R and B letters means the LCUs Radii-Cal and Bluephase G2 respectivelly.

Figure 2. Failure modes distribution of the immediate bond strength test.

Table 2. Means and standard deviation for the one-year long-term microtensile bond strength values for the groups tested.

Adhesives	**One-year bond strength (Mpa)**	
	Bluephase G2	Radii Cal
CQ/DMAEMA	40.9 (6.3) Ac	43.7 (5.9) Ab
PPD/DMAEMA	31.1 (7.8) Ad	43.4 (10.3) Bb
CQ/PPD/DMAEMA	32.6 (6.7) Ad	48.1 (5.2) Bb
BAPO/DMAEMA	56.3 (6.4) Ab	62.2 (12.4) Ba
BAPO	70.4 (6.2) Aa	67.9 (3.6) Aa
CQ/BAPO/DMAEMA	48.4 (6.2) Ac	44.3 (7.7) Ab
SCOTCHBOND MULTI PURPOSE	45.4 (6.1) Ac	49.0 (6.1) Ab

Different uppercase letters in the row and lowercase letters in the column means statistical significance (α=0.05).



M – mixed failure; A – adhesive failure; CSA – cohesive failure in the adhesive layer; CR – resin cohesive failure; CD – dentin cohesive failure. R and B letters means the LCUs Radii-Cal and Bluephase G2 respectivelly.

Figure 3. Failure mode distribution of the one-year long-term bond strength values.

Discussion

Alternative photoinitiators, such as PPD and BPO, are formulated in dental adhesives with an attempt to enhance the optical and physical-mechanical properties, when compared to the conventional CQ/amine system. Enhancing the curing performance and selected properties of dental adhesives consequently decrease the degradation by hydrolysis for these resins, thus, reducing the necessity of replacing restorations. In this sense, this study evaluated the immediate and long-term µTBS of hydrophobic resins from three-step etch-and-rinse adhesives.

The first hypothesis tested was partially accepted, since the BAPO-containing adhesive presented higher bond strength values than the CQ. PPD/amine did not reached the µTBS similar to the conventional photo-initiator. This may be occured especially by the molecule photolysis of the carbono-phosphorus bond which is a fast reaction, generating benzoyl and phosphonyl radicals, which are both extremely reactive and capable of initiating vinyl monomer polymerization (Majima *et al.*, 1991; Medsker *et al.*, 1998). Due to the interaction of the carbonyl groups from BAPO with the central phosphonyl group it generates higher free radicals production than for CQ/amine or PPD/amine systems (Rutsch *et al.*, 1996) and in consequence, the higher monomer conversion leads to a higher bond strength value due to the monomer entrapment inside the hybrid layer.

In the present study, all tested resins showed a decrease in the bond strength values. As it is known, the degradation of the bonded interface can be promoted by either the substrate conditions or the polymeric conditions (Reis *et al.*, 2013). The polymer matrix of the adhesives systems shows the presence of hydrolytically susceptible groups, such as ester and urethane, as well as hydroxyl, carboxyl and phosphate groups (Malacarne *et al.*, 2006). Water can prone the polymer network (Moraes *et al.*, 2008), and the organic bonding are cleaved. When the adhesive is immersed in water, the resin matrix softens, decreasing the frictional forces between the polymeric chains (Ferracane *et al.*, 1998), with posterior weakening of the bonded interface.

PPD have been studied as a promising substitute for CQ. In the present study, the PPD/amine adhesive, regardless of the LCU, showed a poor µTBS when compared to the other experimental adhesive resins and the control group. Conventionally, PPD is considered a Norrysh type I photo-initiator, which the polymerization reaction undergo a unimolecular bond cleavage upon light irradiation to yield free radicals (Albuquerque *et al.*, 2013; Brandt *et al.*, 2013). However, as shown in this study, for the neat hydrophobic resin using the organic matrix BisGMA/HEMA (60/40 wt%), the photo-cleavage expected in addition to the conventional redox photoinitiation by the hole of DMAEMA, PPD was not sufficient to guarantee an adequate bod strength, showing inferior results when compared to CQ/DMAEMA systems and the adhesives containing BAPO (Sun and Chae, 2000; Shroeder *et al.*, 2007). PPD was only tested with the presence of a co-initiator, because differently from BAPO, PPD photo-cleavage between the carbonyls reaction by itself does not promote a satisfactory carbon double bond conversion, needing the presence of a co-initiator to allow the formation of free radicals, such as the conventional CQ/amine systems (Brandt *et al.*, 2013).

The second hypothesis tested was partially accepted, since at the 1-year bond strength evaluation PPD/amine, CQ/PPD/amine and BAPO/amine light cured with Radii-Cal showed higher values when compared to the groups photoactivated by the polywave LED. Even with the standardized energy dose, the monowave LED had 60s of photoactivation compared to the 40s of the polywave LCU. Even if we know that the reciprocity low is very used to cure dental polymers and the long lasting time used by the monowave LED Radii-Cal must have promoted a higher increase of temperature and consequently promoted better bond strength results (Neumann *et al.*, 2006; Brandt *et al.*, 2013)

The formulation of adhesives containing BAPO and PPD should be encouraged, in order to evaluate the impact of these adhesives also in another types of systems, such as 2-step etch-and-rinse and the self-etch categories. Further studies analyzing another physical properties, such as degree of conversion, yellowingmarginal adaptation and dentin permeability of the polymer network should be performed evaluate the inclusion of alternative photo-initiators in the adhesive composition.

Conclusion

The BAPO containing adhesives showed an enhanced bond strength values when compared to the traditional CQ/amine systems or PPD/amine. Thereafter, the adhesives formulated with BAPO are less jeopardized by the long-term hydrolytic degradation for one year. Also, both polywave and monowave LEDs well indicated to photocure dental adhesives containing CQ, PPD and BAPO as photo-initiators.

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CONSIDERAÇÕES GERAIS

No presente estudo avaliou-se propriedades físicas, permeabilidade dentinária e adaptação marginal de adesivos dentais experimentais contendo fotoiniciadores alternativos (PPD e BAPO), sozinhos ou em associação com a canforoquinona, fotoativados por duas fontes de luz LED. Inicialmente, foi realizado o ensaio de grau de conversão após 5 minutos da fotoativação, e observou-se que os adesivos contendo BAPO ou BAPO/DMAEMA juntamente com o adesivo controle, fotoativados pelo Bluephase G2, possuíram maior GC comparados aos demais grupos. Além disso, quando fotoativados pelo Radii, todos os adesivos contendo BAPO e o controle mostraram maiores valores de GC comparados aos outros grupos. Não houve diferença entre as fontes de luz ($p \geq 0.05$). O BAPO é um fotoiniciador que age por foto-clivagem, ou seja, a luz incide sobre a molécula e formam dois radicais livres que vão agir para acontecer a fotopolimerização (NEUMANN *et al.*, 2006). Por outro lado, a luz quando atinge a CQ, esta se torna excitada e sensibiliza a amina terciária que libera somente um radical livre por molécula para realizar a reação de polimerização (PARK, 1999; BRANDT 2010; BRANDT *et al.*, 2013). Sendo assim, os adesivos contendo BAPO provavelmente, por possuírem mais radicais livres iniciadores da reação promoveríam maior GC para a resina adesiva. Já os adesivos formulados com PPD, apesar de agirem por foto-clivagem, somente liberam um radical, possuindo assim valores de GC semelhantes à CQ. (PARK, 1999; BRANDT *et al.*, 2013). O fato de o espectro de emissão da luz azul pelas duas fontes de luz ser mais próximo do pico de absorção da

CQ não permite haver diferença na conversão monomérica fotoativando-se tanto com o LED de pico único quanto com o LED de múltiplos picos.

Realizando-se o ensaio de GC 24hs após a polimerização do adesivo, tem-se que as blendas formuladas com fotoiniciadores alternativos (BAPO, BAPO/DMAEMA, PPD/DMAEMA), além do adesivo controle, quando fotoativados com o LED de múltiplos picos, mostraram maiores valores de GC comparados aos demais grupos. No entanto, quando os adesivos foram fotoativados com o Radii, não houve diferença entre os grupos, exceto entre o controle e o adesivo da associaçãoo CQ/BAPO. O LED Bluephase (LED de múltiplos picos, poliondas ou de 3º geração) possui 3 LEDs que emitem a luz azul e um LED acessório que emite luz próxima à região do ultravioleta (próximo de 410nm), o que sensibilizaria de maneira mais efetiva tanto o BAPO quanto o PPD (NEUMANN *et al.*, 2005; PRICE *et al.*, 2005). Já o Radii, por possuir somente um LED emitindo luz no espectro do pico de absorção luminosa da canforoquinona, polimeriza de maneira mais uniforme os adesivos experimentais do presente estudo.

Os testes flexurais (resistência à flexão e módulo de elasticidade) foram realizados de maneira que pudessem predizer a resistência da resina adesiva bem como a sua rigidez relativa de maneira semelhante às normas da ISO 4940, exceto para a dimensão dos espécimes. Os espécimes foram reduzidos, tornando-se então ensaio de mini-flexão e módulo mini-flexural, já que os espécimes possuíram dimensões de 7mm de comprimento x 2mm de largura x 1mm de espessura. Isso favorece a confecção dos espécimes com uma única fotoativação, de maneira semelhante do que ocorreria na prática clínica diária. De maneira geral, tanto para o Bluephase quanto para o Radii, os adesivos contendo BAPO e o adesivo controle apresentaram maiores valores de resistência fleural, evidenciando o maior GC dos adesivos formulados com esses fotoiniciadores. De maneira semelhante, o módulo de elasticidade apresentou as mesmas características quando comparado aos adesivos contendo PPD e CQ.

Em uma análise dinâmica do comportamento e desenvolvimento da polimerização dos adesivos do presente estudo por meio da cinética de polimerização, observou-se que os adesivos contendo BAPO e BAPO/DMAEMA apresentaram reação de polimerização com taxa de polimerização ocorrendo mais rápida quando comparados os demais grupos. Além disso, essas duas blendas adesivas mostraram em 5 minutos após a fotoativação, as maiores médias de GC, independentes da fonte de luz utilizada. Esse resultado é interessante, já que uma das grandes preocupações da inclusão de fotoiniciadores alternativos em sistemas adesivos dentais é se qualquer fonte de luz LED poderia ser utilizada para uma polimerização satisfatória (PRICE *et al.*, 2005; IKEMURA *et al.*, 2008). Por meio do presente estudo, observou-se que a conversão monomérica dessas resinas adesivas é conseguida de maneira adequada, tanto fotoativando-se com o LED de pico único quanto com o LED poliondas.

O sistema canforoquinona/amina é o sistema de fotoiniciação mais utilizado em adesivos odontológicos (RUEGGEBERG *et al.*, 1999; STANSBURY *et al.*, 2000; BRANDT *et al.*, 2013). Contudo, a canforoquinona é um material da cor amarelo vivo e, quando em grandes quantidades, o polímero formado final pode apresentar certo grau de amarelamento. O BAPO e PPD, fotoiniciadores alternativos são menos amarelos que a canforoquinona, o que pode influenciar nas propriedades estéticas de restaurações em dentes anteriores. No presente estudo, os adesivos contendo somente BAPO ou PPD/amina conseguiram reduzir significativamente o grau de amarelamento dos adesivos testados, independente da fonte de luz utilizada para a fotoativação.

A água, presente nos túbulos dentinários, pode degradar a matriz polimérica do adesivo polimerizado. Sendo assim, os adesivos que atuam sobre a dentina precisam realizar bom selamento dentinário, além de impedir a permeabilidade da própria camada de adesivo, o que facilitaria a degradação da interface adesiva. Para a correta avaliação desses parâmetros, avaliou-se as propriedades de sorção e solubilidade em água, além do selamento dentinário promovido pelo sistema adesivo. Quando fotoativados com o LED de pico único Radii-Cal, os adesivos experimentais apresentaram os mesmos percentuais de selamento dentinário. Utilizando-se o Bluephase G2, obteve-se um resultado similar, exceto para o adesivo CQ/amina e PPD/amina, os quais apresentaram menor selamento dentinário. Provavelmente, isso se deveu ao tempo de exposição luminosa para cada uma das fontes de luz. Para padronizar a mesma dose de energia, o adesivo era fotoativado por 40s com o Bluephase G2 e com o Radii por 60s. Sabe-se que mesmo padronizando a dose de energia, uma irradiância menor promove menor formação de ligações cruzadas do polímero, o que favoreceria a maior passagem de água no adesivo e porcentagem menor de selamento dentinario, aumentando-se a permeabilidade dentinária. (Cadenaro *et al.*, 2005; Sá *et al.*, 2012). Ainda, a sorção de água permaneceu praticamente a mesma entre os adesivos testados, independente da fonte de luz utilizada; entretanto, para os resultados de solubilidade, os adesivos contendo fotoiniciadores alternativos mostraram menores médias.

Para a análise da durabilidade da união em dentina, os resultados imediatos mostraram que o adesivo contendo somente o BAPO obteve o melhor desempenho de união, quando fotoativado com o LED de poliondas. Isso mostra que o BAPO quando fotoativado também pela luz com comprimento de onda próximo do ultravioleta melhora seu grau de conversão e, consequentemente, a união com a dentina. Ainda, quando fotoativado com o Bluephase, os adesivos contendo CQ sozinha ou em associação com o BAPO mostraram excelente desempenho de resistência à microtração. Quando fotoativados com o Radii-Cal, os adesivos contendo CQ sozinha ou em associação com o BAPO apresentaram desempenho similar frente ao ensaio de microtração imediato. Isso mostra que, independente da fonte de luz, os adesivos contendo BAPO são promissores pois conseguem promover adequada conversão monomérica com LEDs de diferentes picos.

Após 1 ano de armazenagem em água, os resultados mostram que, mesmo com leve redução dos valores, os adesivos contendo BAPO e BAPO/amina mostraram maiores valores de resistência de união quando comparados a todos os outros adesivos testados, qualquer que fosse a fonte de luz utilizada. Quando fotoativados com o LED de pico único, mesmo após 1 ano, não houve redução dos valores de resistência da união para os adesivos contendo BAPO e BAPO/amina. Dessa forma, a degradação hidrolítica não foi capaz de deteriorar a matriz polimérica desses sistemas adesivos, garantindo assim maior longevidade do tratamento restaurador.

A adaptação marginal é uma análise importante que visa avaliar a formação de fendas marginais e internas de restaurações em compósito. Portanto, analisando a formação de fendas marginais, observou-se que o adesivo contendo somente BAPO garantiu integridade marginal de 100%, sem formação de fendas, quando fotoativado com LED Bluephase G2. Já para a fotoativação com o Radii-Cal, observou-se que o adesivo comercial Adper Scotchbond Multi-Uso obteve menor formação de fendas, provavelmente por possuir maior concentração de CQ/amina em sua composição, o que torna mais efetiva a formação da matriz polimérica adesiva e maior integridade marginal. Já para a adaptação interna, os adesivos contendo BAPO, juntamente com o controle obtiveram menor formação de fendas.

CONCLUSÃO

O sistema tradicional CQ/amina pode ser substituído por BAPO e PPD na formulação de sistemas adesivos, já que esses fotoiniciadores mantiveram ou melhoraram as propriedades físico-mecânicas, diminuíram o amarelamento e a formação de fendas nesses materiais restauradores, principalmente quando o LED de dois picos foi utilizado.

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COMITÊ DE ÉTICA EM PESQUISA
FACULDADE DE ODONTOLOGIA DE PIRACICABA
UNIVERSIDADE ESTADUAL DE CAMPINAS

CERTIFICADO

O Comitê de Ética em Pesquisa da FOP-UNICAMP certifica que o projeto de pesquisa **"Influência de fotoiniciadores alternativos na durabilidade da união, adaptação marginal e propriedades físico-químicomecânicas de adesivos dentais experimentais fotoativadas por LED"**, protocolo nº 137/2011, dos pesquisadores Mário Alexandre Coelho Sinhoreti e Eduardo José Carvalho de Souza Junior, satisfaz as exigências do Conselho Nacional de Saúde - Ministério da Saúde para as pesquisas em seres humanos e foi aprovado por este comitê em 21/12/2011.

The Ethics Committee in Research of the School of Dentistry of Piracicaba - State University of Campinas, certify that the project **"Influence of alternative photoinitiators on the bond durability, marginal adaptation and physical-chemical-mechanical properties of experimental dental adhesives photocured by LED"**, register number 137/2011, of Mário Alexandre Coelho Sinhoreti and Eduardo José Carvalho de Souza Junior, comply with the recommendations of the National Health Council Ministry of Health of Brazil for research in human subjects and therefore was approved by this committee at 12/21/2011.

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Nota: O título do protocolo aparece como fornecido pelos pesquisadores, sem qualquer edição.
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