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Aplicação de sistemas fotoiniciadores alternativos em compósitos odontológicos.

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

Orientador: Prof. Dr. Simonides Consani

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RESUMO

O presente estudo teve como objetivo investigar a aplicação de sistemas fotoiniciadores alternativos em compósitos odontológicos. Para melhor entendimento, o trabalho foi dividido em três Capítulos. O Capítulo 1 teve como objetivos específicos 1) avaliar a taxa de polimerização máxima (TPmax), grau de conversão (GC), dureza e grau de amarelo (GA) de compósitos contendo canforoquinona (CQ), fenil-propanodiona (PPD) ou a combinação (CQ/PPD) em três diferentes concentrações; 2) avaliar a densidade de potência absorvida (DPabs, em mW/cm^3) pelos sistemas fotoiniciadores (parâmetro utilizado para estimar a correlação entre os espectros de absorção dos fotoiniciadores e o espectro emitido pela fonte de luz). As hipóteses testadas foram: a) PPD e/ ou CQ/PPD poderia reduzir GA e TPmax sem reduzir GC e dureza; b) TPmax, GC e dureza são dependentes da DPabs. TP foi avaliada por calorimetria diferencial de varredura (DSC), GC por espectroscopia transformada de Fourier (FTIR), dureza por endentação Knoop e GA por um colorímetro (eixo *b*). Concluiu-se que: 1) apenas CQ/PPD reduziu a TPmax sem reduzir GC e dureza; 2) uma redução do GA foi possível apenas quando PPD foi utilizada em baixa concentração e 3) TPmax, GC e dureza são dependentes da DPabs. O Capítulo 2 avaliou o efeito da proporção de amina na TPmax, GC, dureza Knoop, sorção de água (Wsr), solubilidade em água (Wsl) e alterações de cor (ΔE) em função do tempo para compósitos formulados com CQ, PPD e CQ/PPD. Foram testadas as proporções fotoiniciador:amina 2:1, 1:1, 1:1.5 e 1:2, em peso. TPmax foi avaliada por DSC, GC por DSC e FTIR, dureza por endentação Knoop, Wsr e Wsl adaptadas da ISO 4049; e ΔE por um colorímetro. Quanto maior a proporção de amina empregada, maior foi GC, TPmax e dureza, e menor foi Wsl, independentemente do fotoiniciador usado. O uso do PPD resultou em piores propriedades do que CQ e CQ/PPD. Diversos fatores afetam ΔE. A maior quantidade de amina usada foi responsável pelos maiores níveis de amarelo para as formulações de CQ e CQ/PPD. Concluindo, o uso do PPD sozinho não foi vantajoso, se comparado com CQ e CQ/PPD; a eficiência do fotoiniciador foi dependente da proporção de amina empregada, independentemente do tipo de fotoiniciador; a quantidade de amina influenciou o GA para compósitos formulados com CQ e CQ/PPD. O estudo descrito no Capítulo 3 verificou a influência dos diferentes sistemas fotoiniciadores (CQ, PPD e CQ/PPD) no desenvolvimento da tensão de polimerização e propriedades resultantes (GC e densidade de ligações cruzadas, DLC) de compósitos restauradores. A hipótese testada foi de que PPD e/ou CQ/PPD poderia reduzir a tensão de polimerização sem reduzir GC e DLC. TPmax foi aferida por DSC e a tensão por um sistema de alavanca (Bioman). GC, avaliado por FTIR, e DLC (medido indiretamente pelo coeficiente inchamento) foram determinados a partir das amostras removidas do Bioman. De acordo com os resultados, pode-se concluir que o sistema CQ/PPD foi capaz de reduzir a taxa máxima de tensão sem reduzir o GC e a DLC.

Palavras-chave: aminas, canforoquinona, fotoiniciador, grau de conversão, PPD, resina composta.

ABSTRACT

The aim of the present study was to evaluate the application of alternative photoinitiators in dental resin composites. The work was divided into two Chapters in order to make the objectives clearer. The specific aims of the Chapter 1 were: 1) to evaluate the maximum rate of polymerization (R_p^{max}), degree of conversion (DC), hardness and yellowing of resin composites formulated with camphorquinone (CQ), phenylpropanedione (PPD) or CQ/PPD at three different concentrations; 2) to evaluate the absorbed power density (PD_{abs}, in mW/cm^3) by the different systems (parameter used to estimate the correlation between photoinitiators' absorption and light emission spectra). The hypotheses tested were: a) PPD and/ or CQ/PPD could reduce the yellowing degree and R_p^{max} without reduction in the DC and hardness; b) R_p^{max}, DC and hardness are directly dependent on the PD_{abs}. Rate of polymerization was evaluated with differential scanning calorimetry (DSC), DC with Fourier transformed infrared spectroscopy (FTIR), hardness with Knoop indentation and yellowing with a chromameter (b axis). According the results, it was concluded that: 1) CQ/PPD reduced the R_p^{max} without affecting DC and hardness; 2) the yellowing reduction by PPD formulations was possible only at low concentration and 3) R_p^{max}, DC and hardness are dependent on the PD_{abs}. The 2nd study evaluated the effect of amine ratio on the R_p^{max}, DC, hardness, water sorption (Wsp), water solubility (Wsl) and color changes (ΔE) over time of composites formulated with CQ, PPD and CQ/PPD. Photoinitiator:amine ratios 2:1, 1:1, 1:1.5 and 1:2, by weight, were used in experimental composites. R_p^{max} wasevaluated with DSC, DC with DSC and FTIR, hardness with Knoop indentation, Wsp and Wsl adapted from ISO 4049; and ΔE with a chromameter. The results showed that the higher the amine ratio, the higher was DC, R_p^{max}, hardness and lower was Wsl, regardless of the photoinitiator type. The use of PPD alone resulted in poorer properties than CQ and CQ/PPD. Many factors seem to affect the ΔE. The higher was the amine ratio, the higher was the yellowing for CQ and CQ/PPD formulations. Thus, it is possible to conclude that the use of PPD alone was not advantageous; the photoinitiator efficiency was dependent on the amine ratio, regardless of the photoinitiator type; and the amine ratio affected the yellowing for composites with CQ and CQ/PPD. The third study evaluated the influence of different photoinitiator systems (CQ, PPD or CQ/PPD) on the stress of polymerization development and composites' resultant properties (DC and crosslinking density, CLD). The hypothesis tested was that PPD and/ or CQ/PPD could reduce the stress development without affecting the final DC and CLD. Besides the DSC evaluation, stress development was checked with a cantilever apparatus (*Bioman*), DC with a FTIR and CLD was indirectly assessed trough the swelling coefficient. The combination CQ/PPD reduced the rate of stress development without reduction on the DC and CLD.

Keywords: amines, camphorquinone, degree of conversion, photoinitiator, PPD, resin composite.

SUMÁRIO

INTRODUÇÃO

Os compósitos fotoativados foram introduzidos no mercado na década de 70, onde os primeiros produtos disponíveis eram ativados por irradiação ultravioleta (UV). Se comparados aos compósitos ativados quimicamente, estes materiais apresentavam diversas vantagens, como por exemplo: 1) dispensavam a mistura entre duas pastas, reduzindo a incorporação de oxigênio no interior da massa e melhorando a distribuição dos iniciadores; 2) possuíam reduzida quantidade de amina, diminuindo o grau de amarelo proveniente do processo de oxidação desta molécula e 3) proporcionavam controle do tempo de presa e 4) de trabalho (RUEGGEBERG, 2002). Entretanto, a irradiação UV tem o potencial de gerar danos oculares e alterações da flora bucal. Além disto, os materiais fotoativados por luz UV apresentavam propriedades físicas e mecânicas insatisfatórias, pois a profundidade de polimerização era um fator extremamente crítico (COOK, 1980; RUYTER & ØYSÆD, 1982).

Conseqüentemente, materiais foram desenvolvidos a partir da utilização de moléculas sensíveis à luz visível (DART *et al.*, 1976; DART & NEMECK, 1978). Além de reduzir a probabilidade de danos biológicos, estes materiais proporcionavam maior profundidade de polimerização e redução do tempo de exposição à luz (RUYTER & ØYSÆD, 1982). Assim, a canforoquinona (CQ) foi adotada como molécula fotoiniciadora (Figura 1) e, desde sua adoção, tem sido utilizada nas formulações de compósitos odontológicos comerciais (SHINTANI *et al.*, 1985; TAIRA *et al.*, 1988; ALVIM *et al.*, 2007).

Basicamente, um fotoiniciador é toda molécula capaz de absorver luz e, como resultado, direta ou indiretamente, gera espécies reativas que podem iniciar a polimerização. De forma geral, as moléculas fotoiniciadoras apresentam um grupamento "carbonila" em sua estrutura, pois este grupamento possui um elétron que pode ser transformados em orbital "anti-união" quando absorve luz no comprimento de onda adequado (STANSBURY, 2000).

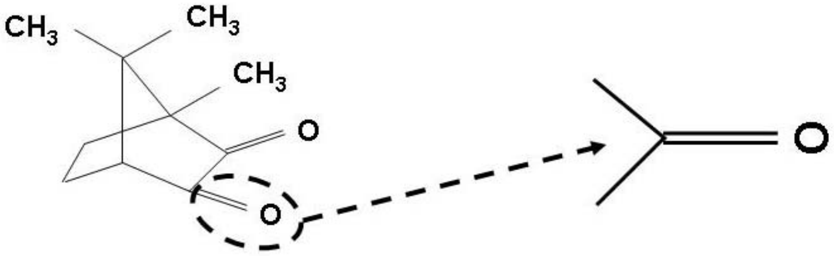

Figura 1: Molécula de canforoquinona – destaque para o grupamento "carbonila".

Quanto ao processo de geração dos radicais livres, os fotoiniciadores podem ser classificados em dois tipos (ANDRZEJEWSKA, 2001):

Tipo I: Geram radicais através de um eficiente processo de clivagem. Ou seja, existe uma quebra da molécula para que haja a formação dos radicais livres. Normalmente, estes sistemas absorvem luz com comprimento de onda em torno de 380 nm. Um exemplo deste grupo de moléculas é o éter metil benzoínico, o qual foi utilizado como sistema fotoiniciador da primeira resina composta disponível no mercado, o Nuva System (Dentsply/Caulk) (RUEGGEBERG, 2002).

Tipo II: Moléculas que necessitam de um co-iniciador para que haja a formação dos radicais livres. Ou seja, para fotoiniticadores do tipo II existe a necessidade de uma molécula que não absorva luz, mas que interaja com o iniciador. Assim, os radicais livres são formados a partir do deslocamento da molécula de hidrogênio do co-iniciador para a molécula fotoiniciadora. Como maior exemplo deste grupo, a canforoquinona.

Basicamente, a canforoquinona absorve luz na região azul do espectro eletromagnético (400-550 nm) e possui pico de absorção máxima em 468 nm. Ao receber luz (energia) neste comprimento de onda, o grupamento carbonila pode passar a um estágio de excitação, chamado "triplete" (Figura 2A), com meia-vida de 0,5 ms (TSAI & CHARNEY, 1969). Neste momento, pode ocorrer a fragmentação da molécula de canforoquinona. Entretanto, como os dois radicais carbonilas presentes na molécula da CQ estão estruturalmente conectados, pode ocorrer uma recombinação da molécula (SUN & CHAE, 2000). Ou seja, a CQ pode retornar ao seu estágio inicial.

Por outro lado, caso a CQ encontre uma molécula "doadora" de átomos de hidrogênio - antes de uma eventual "desativação" do estágio triplete – ocorre a geração de um estágio complexo excitado chamado "exciplexo" (Figura 2B). Neste momento, o co-iniciador "doa" um átomo de hidrogênio (Figura 2C) e, conseqüentemente, gera dois radicais livres (Figura 2D). Entretanto, é apenas o radical amino que inicia o processo de polimerização, enquanto o radical cetila pode até ser um fator de retardo da reação, caso este se una a uma cadeia em propagação, causando terminação prematura (COOK 1992, STANSBURY 2000; CORRÊA 2003).

Apesar de ser um sistema eficiente, a canforoquinona apresenta coloração amarela de grande intensidade (Figura 3a). Assim, postula-se que a sua concentração deveria ser restrita para que não houvesse prejuízos estéticos (TAIRA *et al.*, 1988; RUEGGEBERG, ERGLE & LOCKWOOD, 1997; KALLIYANA KRISHNAN & YAMUNA, 1998; PARK, CHAE & RAWLS, 1999).

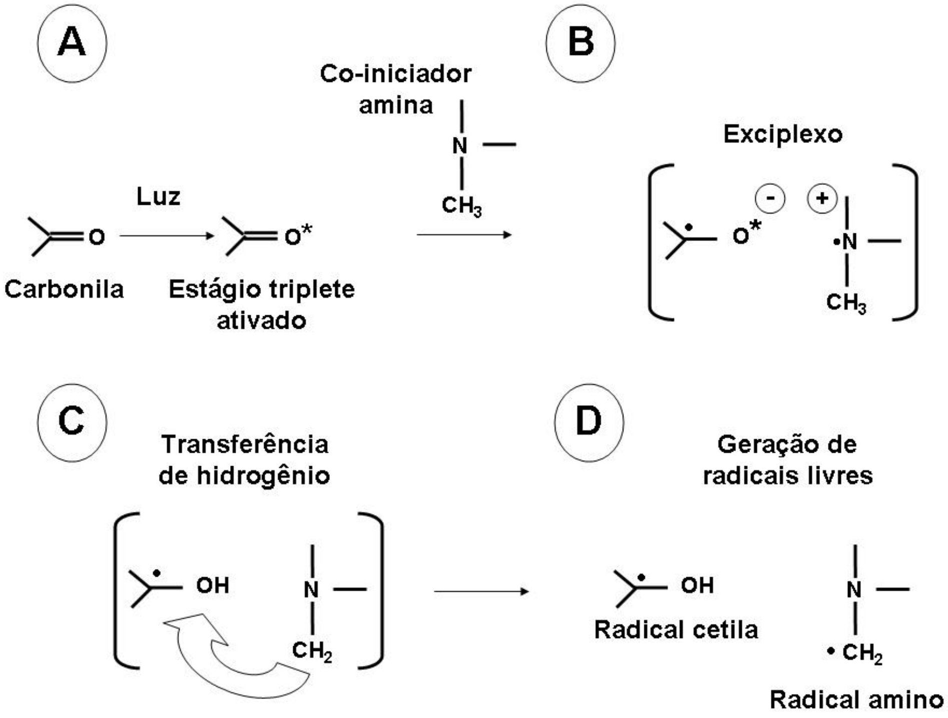

Figura 2: Processo de formação de radicais livres a partir do sistema canforoquinona/ amina.

Desta forma, sistemas fotoiniciadores alternativos têm sido propostos. Basicamente, estes sistemas absorvem luz em comprimentos de ondas menores (pois possuem menor intensidade de amarelo ou mesmo nenhuma), mas com extensões do perfil de absorção para comprimentos de onda visíveis (SUN & CHAE, 2000, NEUMANN *et al.*, 2005, 2006). Em especial, destacam-se o óxido mono-alquil fosfínico (sob nome comercial TPO), já utilizado em compósitos comerciais (UHL et al. 2003, CORRÊA, 2003) e a fenil-propanodiona (PPD) (PARK, CHAE & RAWLS, 1999; SUN & CHAE, 2000).

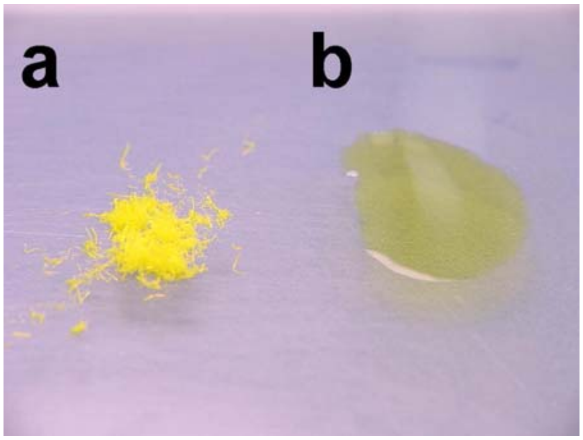

Figura 3: canforoquinona (a) e fenil-propanodiona (b).

A PPD foi sugerida como sistema fotoiniciador alternativo para compósitos odontológicos em 1999 por PARK, CHAE & RAWLS. Segundo estes autores, este líquido viscoso de coloração amarela (Figura 3b) poderia trazer benefícios estéticos e uma melhora na eficiência de polimerização, especialmente quando usado concomitantemente com a CQ.

Além da redução do grau de amarelo (de menor intnsidade do que a CQ), sugere-se um efeito sinérgico resultante de um segundo modo de geração de radicais livres (PARK, CHAE & RAWLS, 1999; SUN & CHAE, 2000). Enquanto a CQ se decompõe por abstração de hidrogênio, típico de um fotoiniciador do Tipo II, sugere-se que a PPD poderia formar radicais livres por dois meios, onde o principal seria através da quebra da ligação entre as moléculas de carbono dos grupos carbonilas (Figura 5), típico de um fotoiniciador Tipo I (STANSBURY, 2000). Adicionalmente, a combinação CQ/PPD poderia promover um maior espectro de absorção, também aumentando a eficiência do sistema fotoiniciador (PARK, CHAE & RAWLS, 1999). No entanto, este efeito sinérgico ainda é motivo de controvérsia (NEUMANN *et al.*, 2006).

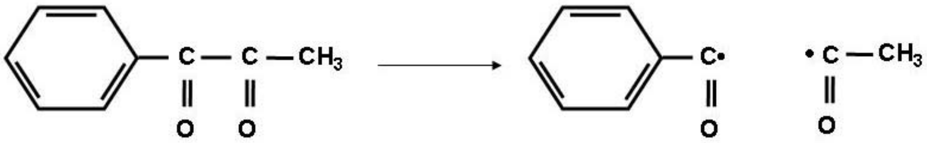

Figura 5: Formação de radicais livres a partir da PPD.

Até o momento, não existem dados reais que provem a redução do grau de amarelo quando a PPD é empregada. Além disso, se por um lado a absorção de luz em menores comprimentos de onda pode trazer benefícios estéticos, problemas podem surgir em função da falta de correlação entre a absorção do sistema fotoiniciador e a emissão da (s) fonte (s) de luz utilizada (s) (NEUMANN *et al.*, 2005, 2006; BRANDT, 2007). Assim, o uso de maiores concentrações poderia ser uma forma de contornar uma eventual queda da correlação entre os espectros de absorção, do fotoiniciador, e de emissão, da fonte de luz. Entretanto, pouco se sabe sobre a influência da concentração da PPD no polímero resultante, bem como do próprio processo de geração de radicais livres e afinidade com co-iniciadores.

Recentemente, estudos mostraram que compósitos formulados com a PPD tendem a promover uma menor taxa de reação do que a CQ sem que haja comprometimento do grau de conversão final (ASMUSSEN & PEUTZFELDT, 2002; EMAMI & SÖDERHOLM, 2005). Segundo estes autores, esta característica poderia reduzir a tensão gerada pelo processo de polimerização. No entanto, como os próprios autores afirmam, esta é apenas uma hipótese, pois não existem dados reais mostrando este benefício.

PROPOSIÇÃO

Pode-se observar que muitas dúvidas ainda existem a respeito das conseqüências da aplicação de diferentes sistemas fotoiniciadores em compósitos odontológicos. Desta forma o presente estudo teve as seguintes proposições[*]:

1. Avaliar a taxa de polimerização, grau de conversão, dureza e grau de amarelo de compósitos experimentais contendo diferentes sistemas fotoiniciadores (CQ, PPD ou CQ/PPD) empregados em diferentes concentrações. Avaliar a densidade de potência absorvida (parâmetro utilizado para correlacionar os espectros de absorção e emissão) por estes sistemas. Correlacionar a densidade de potência absorvida (PD_{abs}) com a taxa de polimerização, grau de conversão e dureza.
2. Avaliar o efeito da proporção de amina na taxa de polimerização, grau de conversão, dureza, sorção de água, solubilidade em água e alterações de cor, em função do tempo de estocagem em água, de compósitos formulados com CQ, PPD ou CQ/PPD.
3. Avaliar a tensão de polimerização gerada por diferentes sistemas fotoiniciadores (CQ, PPD e CQ/PPD) e verificar as características do polímero formado (grau de conversão e densidade de ligações cruzadas).

[*] Este trabalho foi realizado no formato alternativo, com base na deliberação da Comissão Central de Pós-Gradução (CCPG) da Universidade Estadual de Campinas (UNICAMP).

CAPÍTULO 1

INFLUENCE OF PHOTOINITIATOR TYPE ON THE RATE OF POLYMERIZATION, DEGREE OF CONVERSION, HARDNESS AND YELLOWING OF DENTAL RESIN COMPOSITES.

ABSTRACT

Objectives: To evaluate the degree of conversion (DC), maximum rate of polymerization (R_p^{max}), Knoop hardness (KHN) and yellowing (b-value) of resin composites formulated with phenylpropanedione (PPD), camphorquinone (CQ), or CQ/PPD at different concentrations. The hypotheses tested were (i) PPD or CQ/PPD would produce less R_p^{max} and yellowing than CQ alone without affecting DC and KHN, and (ii) R_p^{max}, DC, and KHN would be directly related to the absorbed power density (PD_{abs}). **Methods:** CQ/amine, PPD/amine and CQ/PPD/amine were used at low, intermediate and high concentrations in experimental composites. Photoinitiator absorption and halogen-light emission were measured using a spectrophotometer, R_p with differential scanning calorimetry (DSC), DC with DSC and FTIR, KHN with Knoop indentation; and color with a chromameter. The results were analyzed with two-way ANOVA/Student-Newman-Keul's test ($p<0.05$). Correlation tests were carried out between PD_{abs} and each of DC, R_p^{max} and KHN. **Results:** The PD_{abs} increased with photoinitiator concentration and PPD samples had the lowest values. In general, maximum DC was comparable at intermediate concentration, while R_p^{max} and KHN required higher concentrations. DC was similar for all photoinitiators, but R_p^{max} was lower with PPD and CQ/PPD. PPD produced the lowest KHN. Yellowing increased with photoinitiator concentration. PPD did not reduce yellowing at intermediate and/or high concentrations, compared to CQ-formulations. PD_{abs} showed significant correlations with DC, R_p^{max} and KHN. **Conclusion:** PPD or CQ/PPD reduced R_p^{max} in experimental composites without affecting the DC. The use of PPD did not reduce yellowing, but reduced KHN. DC, R_p^{max} and KHN were dependent on PD_{abs}.

1. INTRODUCTION

Camphorquinone (CQ) has been largely used as a photoinitiator since the introduction of visible-light activated resin composites. However efficient this photoinitiator might be, its association with an electron/proton donor substance, usually a tertiary amine, may increase reactivity [1-3]. Absorption of light by CQ typically leads to the creation of two excited states: i) the “singlet state”, which does not involve reversal of electron spin, and ii) the “triplet-state”, which is the one relevant to free radical formation and which has a very short half-life [4]. While in the triplet state, the CQ molecule may interact with an amine molecule and generate an excited state complex, the “exciplex”. Thus, the CQ abstracts a hydrogen atom from the tertiary amine resulting in free radical formation [2].

One factor that influences radical formation in CQ/amine systems is the concentration of the photoinitiators, which are known to vary among commercial brands [5, 6]. There is evidence that higher concentrations of photoinitiators improve the degree of conversion and mechanical properties of the formed polymer [7-13]. Unfortunately, above a certain threshold, no benefits are observed [9, 14] and may affect aesthetics due to CQ’s yellow color [10, 11, 15, 16]. Although the yellowing might be reduced during the photoactivation process, part of the photoinitiator may remain unreacted due to insufficient irradiation [17] or other physical effects, such as the inner shielding effect [14]. Therefore, the restoration could still be yellowish and non-acceptable esthetically [17, 18].

Studies have presented alternative photoinitiators (e.g, PPD) that could be used alone or in combination with CQ to reduce the “yellowing effect” in dental resins. The absorption peak of these molecules is at shorter wavelengths than CQ and they tend to be less yellow [2, 16, 19-21]. However, the literature on these alternative molecules is still poor and there is no consensus as to their potential for “yellowing” reduction or to the effect on the structure of the formed polymer.

The photoinitiator phenylpropanedione (PPD) has shown promising results as an alternative system for light-activation of dental resins. Besides the claimed advantage of less yellowing [16], PPD produces a lower rate of polymerization without affecting the final degree of conversion compared to CQ containing formulations [22-24]. It has been suggested that the rate of polymerization may affect the polymerization stress development [25], but this is a matter of controversy [26]. The polymer formed at lower rates has been suggested to be more linear, although no consensus about this matter has been reached either [27-29]. Consequently, PPD-formulations could be useful for reducing stress within the material and at the resin-tooth interface.

However, since the light curing units are optimized for curing CQ, and alternative photoinitiators absorb light at shorter wavelengths than CQ, these units may not be suitable for use with alternative photoinitiators [19]. Indeed, the low rate of reaction reported with the use of these photoinitiators has been related to lower light absorption [23]. One way to overcome this problem, as hypothesized by Neumann *et al.* [19], would be to increase the curing time or to design materials with higher concentrations of the alternative photoinitiators. However, there are only a few studies that deal with the influence of PPD concentration on the polymerization rate and on the structure of the resultant polymers [24].

Apart from the photoinitiator concentration and the irradiation protocol, certain characteristics related to the chemistry of the molecule itself can also affect curing initiation. The photoinitiator molecule must have a high molar extinction coefficient, which is defined as the absorption per unit length divided by the molar photoinitiator concentration of the solution. The best photoinitiators have high absorptions at low concentrations [2]. However, as previously mentioned, if the light curing unit does not emit sufficient light in wavelenths that are absorbed by the photoinitiator, then the polymerization process may be affected. Thus, considering solely the relationship between light emission and absorbance (since the chemical mechanism of free radical generation [20] as well as the optical properties [30] may also play a role in the process), it is the effective absorbed energy that influences the photoinitiation process [31]. For that reason, it is important to describe both the molar extinction coefficient as well as the absorbed power density (PD_{abs}) when studying different photoinitiator systems.

The objective of the present study was to evaluate the degree of conversion (DC), Knoop hardness (KHN), maximum rate of polymerization (R_p^{max}), and the “yellowing-effect” (assessed through the b-value of the CIELab color system) of resin composites activated by different photoinitiator systems. These parameters were studied as a function of different photoinitiator concentrations. The PD_{abs} was studied to understand how well the light curing unit spectrum related with the photoinitiator’ absorption spectra, and to check the correlation between the reaction kinetics and final polymer structure with the PD_{abs}. The hypotheses tested were that:

i) PPD, by itself or combined with CQ, could promote comparable physical/mechanical properties as those achieved with the use of CQ alone, but with reduced "yellowing effect" and reduced rate of polymerization, and

ii) the maximum rate of polymerization (R_p^{max}), degree of conversion (DC) and hardness are directly dependent on the PD_{abs}.

2. MATERIALS AND METHODS

2.1 Materials:

The monomers 2,2 bis[4-2(2-hydroxy-3-methacroyloxypropoxy)phenyl] propane (Bis-GMA, Esstech, Essington, PA, USA) and triethyleneglycol dimethacrylate (TEGDMA, Esstech) were mixed in equal parts by weight. Two photoinitiators were used to make the resin photo-curable: CQ (Polysciences Inc., Warrington, PA, USA), 1-phenyl-1,2- propanedione, PPD (Aldrich Chem. Co., Milwaukee, WI, USA), and a combination of both in equal parts by weight. A tertiary amine, ethyl 4-dimethylaminobenzoate (EDMAB, Avocado, Heysham, Lanchire, UK), was added to produce a total photoinitiator to total amine ratio of 2:1 (by weight). Three concentrations were tested and named "Low", "Intermediate" or "High" (Table 1). An inhibitor, 2,6-di-*tert*-butyl-4-methyl-phenol (BHT, Aldrich), was added at 0.05 wt%.

Inorganic silanated fillers of strontium glass and fumed silica in a 15:1 ratio by weight were added at 60 wt%. All the components were mechanically mixed at 1300 rpm

(DAC 150 Speed Mixer, Flacktek, Landrum, SC, USA) for 1 minute to produce a homogeneous paste. All materials were prepared and handled under safe yellow light.

All photoactivation procedures were carried out with a quartz-tungsten-halogen (QTH) light curing unit (LCU) (VIP, Bisco Inc., Schaumburg, IL, USA).

2.2 Methods:

2.2.1 Light Curing Unit emission and photoinitiators absorption spectra readings

The total light curing unit power output (mW) was measured with a power meter (Powermax 5200, Molectron, Portland, OR, USA). The irradiance (*E*), in mW/cm^2, was determined by dividing the power output by the area of the light guide. The power output measurement was repeated with the differential calorimeter cap used with the DSC to simulate the irradiance used inside the calorimeter chamber (section 2.2.3). The VIP emission spectrum was determined in the range 350-550 nm range using an integrating sphere (Labsphere Inc., North Sutton, NH, USA) connected to a spectrofluorometer (SPEX Fluorolog-3, Jobin Yvon Inc., Edison, NJ, USA).

Approximately 0.5 cm^3 of resin (before filler addition) was placed in a 1-mm-thick, custom-made, glass-slide cuvette. Absorption spectra of the photoinitiators were measured using a UV-Vis diode array spectrophotometer (Hewlett Packard 8452A, Palo Alto, CA, USA) over the range of 350-520 nm.

2.2.2 Molar extinction coefficient and total absorbed energy calculation

The molar extinction coefficients (mm^{-1} mol^{-1} L) were calculated from the absorbance values using the Beer–Lambert law,

$$A(\lambda) = \varepsilon(\lambda)\,[c]\,l$$

where $A(\lambda)$ is the spectrophotometer absorbance at each wavelength, $\varepsilon(\lambda)$ is the molar extinction coefficient, $[c]$ is the molar concentration of the photoinitiator and l is the optical pathlength through the cuvette . Therefore, the molar extinction coefficient is

$$\varepsilon(\lambda) = A(\lambda) / [c]\, l.$$

The absorption coefficient $\mu_a(\lambda)$ *has units of [1/cm] and is given by*

$$\mu_a(\lambda) = -\ln(10)\, \varepsilon(\lambda)\, [c]$$

Absorbed Power Density (PD_{abs}):

The absorbed power density (in mW/cm^3) was calculated as

$$PD_{abs} = \int E(\lambda) \mu_a(\lambda)\, d\lambda$$

where $E(\lambda)$ is the spectral irradiance of the light curing unit in $(mW/cm^2)/nm$ emitted from the VIP LCU, $\mu_a(\lambda)$ is the photoinitiator absorption coefficient in cm^{-1}, and $d\lambda$ is a differential wavelength (nm). The $E(\lambda)$ values used for the PD_{abs} calculation were those obtained when the light guide was positioned close to the power meter.

The $\varepsilon_{(\lambda)}$ was calculated at each 2 nm wavelength interval to calculate PD_{abs}. Special attention was taken at the photoinitiators' absorption peaks, as demonstrated in the "Results" section.

2.2.3 Differential Scanning Calorimetry (DSC)

Real-time polymerization was assessed by differential scanning calorimetry (DSC). Ten milligrams of composite (approximately 130 µm thick) were photoactivated in standard aluminum crucibles (Perkin-Elmer Inc., Wellesley, MA, USA) in the DSC chamber (DSC 7, Perkin-Elmer Inc., Wellesley, MA, USA) under nitrogen gas purge (20 psi) at 25°C (n=3). Each specimen was irradiated in the DSC three times. Each DSC thermogram comprised 40 second irradiance at 235 mW/cm^2. The peak in the first thermogram represented the exotherm generated by the polymerization of the material plus the heat generated by the light curing unit. The peaks in the next two thermograms represented only the heat generated by the light curing unit on the polymerized material (the second two thermograms were essentially equivalent and lower than the first). The area under each heat flow peak was integrated. The isothermal heat of reaction was obtained by subtracting the average of the peak areas in the last two thermograms from the area under of first peak [23, 32]. Real-time degree of conversion (DC) was calculated by dividing the cumulative heat flow (registered at one data point per second) with the theoretical heat release per mole of reacted carbon double bonds (56 kJ/mol). The maximum rate of conversion (R_p^{max}) was found by taking the first derivative of the DC with respect to time.

2.2.4 Knoop hardness and Fourier Transformed Infrared (FTIR) spectroscopy

50±0.5 mg of the experimental composite was applied and light activated in standard aluminum crucibles in the DSC chamber under the same conditions as described above (n=3). However, specimens were photoactivated with a single 40 sec exposure.

As the samples exhibited a small concavity on their upper surface after the photoactivation procedure, Knoop hardness was measured on the bottom surface. Therefore, a razor blade was used to cut away the aluminum pans and expose the entire sample. To avoid any abrupt deformation of the sample - with consequent interferences in the Knoop hardness readings - the concavity was filled with slow-cure epoxy resin (Buehler epoxide, Buehler, Lake Bluff, IL, USA) and stored in dark containers at room temperature (25±1^{o}C) for 24 hrs. Then, Knoop hardness measurements were taken with a 100 g load applied for 20 s (Kentron Hardness Tester, Torsion Balance Co., Clifton, NJ, USA). Five indentations per surface were averaged for each specimen. The same specimens were then used for the DC analysis. As the intention was to analyze hardness and degree of conversion under the same conditions, the FTIR measurements were also taken from the bottom surface. Therefore, small chips of resin composite removed with a scalpel from the surface of the sample were placed on a KCl crystal for transmission FTIR (DS20/XAD microscope, Analect Instruments, Irvine, CA, USA). Thirty scans were taken at 8 cm^{-1} resolution. Five measurements were made with chips removed from different regions of the sample and an average DC value was calculated. The paste of the uncured composite was similarly tested. DC was calculated from the ratio of the C=C peak from the methacrylate group to that of the unchanging C…C peak from the aromatic ring for the uncured and cured specimens using standard baseline techniques [33].

2.2.5 "Yellowing effect" level measurements

Specimens were prepared by placing the composite in a stainless steel mold (8.7 mm diameter and 1 mm thickness) sandwiched between Mylar strips. The composite was photoactivated for 40 sec at 514 mW/cm^2, directly though the Mylar. The specimens were stored dry in a dark container for 24 hours at room temperature ($25\pm1^{o}C$). Then, the CIELab parameters were measured with a chromameter (Minolta, Corp., Ramsey, NJ, USA). The b-axis data was used to quantify the shift in yellow wavelengths, i.e. the higher the b-value, the higher the yellowing effect.

2.3 Statistical analysis:

The results for each test were analyzed by two-way analysis of variance (ANOVA) followed by Student Newman Keul's test (significance level of 5%).

Pearson's correlation tests ($p<0.05$) were done to analyze the relationship between PD_{abs} and DC (from DSC and FTIR), R_p^{max} and hardness.

3. RESULTS

3.2.1 Light Curing Unit emission and photoinitiators absorption spectra

The VIP light curing unit irradiance (when set at 600) was approximately 510 mW/cm^2 when the light guide was positioned close to the power meter sensor. Because of the glass window and the distance between the light tip and the aluminum pan, the irradiance value decreased to roughly 230 mW/cm^2 in the DSC unit. The wide spectral range (364 – 520 nm) of the VIP is shown in Figure 1a.

Figure 1b shows the absorption coefficient as a function of the wavelength for the different photoinitiators. While CQ has a maximum absorption at 470 nm, the absorption peak for PPD occurred at 392 nm. The mixture CQ/PPD had an absorption peak at 452 nm.

3.2.2 Molar extinction coefficient and absorbed power density

The molar extinction coefficient ($\varepsilon_{(\lambda)}$) and PD_{abs} are presented in Table 2. Since the $\varepsilon_{(\lambda)}$ is a constant, the value is independent of the concentration. As expected, a strong linear relationship was established between concentration (mol/L) and absorption (cm^{-1}) for both photoinitiators (CQ, $r = 0.9992$; and PPD, $r = 0.9980$). The two photoinitiators (CQ and PPD) showed similar ε values (Table 2). On the other hand, the PD_{abs} increased with the concentration and PPD presented the lowest value, regardless of the concentration.

3.2.2 Differential Scanning Calorimetry (DSC)

Table 3 shows the overall results for DC (DSC and FTIR), R_p^{max}, KHN and yellowing.

Based on the DSC evaluation, the DC achieved with the intermediate and high concentrations of photoinitiator were greater than that obtained with the low concentration for PPD and CQ/PPD. For CQ, the concentration did not affect the final DC. For a given concentration, there were no statistical differences among the tested photoinitiators. Conversely, the R_p^{max} increased significantly with the concentration, regardless of the photoinitiator. As for R_p^{max}, the photoinitiators consistently ranked as follows: CQ > CQ/PPD > PPD.

Figure 2 shows R_p curves obtained in real-time by the DSC method. The reaction peak-time (time at R_p^{max}) occurred at approximately 6.0 s, with the exception of CQ at intermediate (5.3 s) and high (5.0 s) concentrations. Instead of a defined peak, the R_p^{max} for PPD was observed between 6 and 10 seconds. The DC value at R_p^{max} was ≈ 15 %, with the exception of PPD at low concentration (DC ≈ 7 % at R_p^{max}).

3.2.3 Knoop hardness and DC

The hardness values increased with the photoinitiator concentration, except for CQ which did not show significant differences between the intermediate and high concentrations (Table 3). Composites containing PPD had lower KHN than those containing CQ, regardless of the concentration tested. Composites containing CQ and the CQ/PPD mixture produced comparable KHN values only at the high concentration.

Intermediate and high concentrations produced higher DC, as determined by FTIR, than the low concentration in the CQ and PPD formulations. For the combination CQ/PPD, the increase in DC was ranked as: high > intermediate > low. For a given concentration, there were no statistical differences among the photoinitiator types, similar to what was shown with the DSC.

3.2.4 “Yellowing effect” level

The yellowing effect always increased as the photoinitiator concentration increased, regardless of the photoinitiator type (Table 3). At the low concentration, the samples containing PPD showed the lowest mean values for the b parameter. However, at the intermediate and high concentrations, the samples containing PPD presented the highest yellowing effect. Samples containing CQ and CQ/PPD did not statistically differ at the low and the intermediate concentrations. At the high concentrations, CQ/PPD produced greater yellowing than CQ.

3.2.5 Correlations

The Pearson’s correlation tests demonstrated positive and significant relationships between PD_{abs} and DC from the DSC ($r = 0.716$, $p = 0.030$), PD_{abs} and R_p^{max} ($r = 0.943$, $p = 0.000$), PD_{abs} and Knoop hardness ($r = 0.953$, $p = 0.000$) and PD_{abs} and DC from the FTIR ($r = 0.873$, $p = 0.002$).

4. DISCUSSION

The purpose of the present study was to determine how different photoinitiator systems used at different concentrations, but at a constant photoinitiator/amine ratio, would affect DC, R_p^{max}, Knoop hardness and yellowing of experimental resin composites, and to describe the influence of the true light absorption (the power density absorbed) in the reaction kinetics (R_p) and final structure of the polymer (indirectly represented by DC and hardness).

As expected, DC, R_p^{max} and hardness tended to increase as the photoinitiator concentration was increased due to the greater amount of molecules available for reaction. This was probably due to the higher PD_{abs}, as demonstrated by the significant correlations between PD_{abs} and each of the variables, which is in agreement with previously reported data [9, 25]. However, it has been shown that this relationship between concentration and efficiency may hold up to a certain threshold, above which excess CQ may decrease conversion. This effect has been related to either radiation attenuation through the film by CQ absorption through a phenomenon known as the inner shielding effect [3,14], or to high rates of primary radical termination, which in turn were caused by the high rates of initiation [8]. Indeed, it has been shown that the DC of an experimental resin composite increased as CQ concentration increased from 0.3 to 0.6 wt% of the total resin matrix, and that above this limit, DC actually decreased [12].

The mechanism of free radical formation in polymers varies according to the photoinitiator system used. For instance, CQ and PPD present dissimilar behavior: while CQ operates by proton abstraction, PPD undergoes photo-cleavage and proton abstraction [21]. Moreover, the light absorption peaks for these photoinitiators occur at different wavelengths, and therefore, their combination produces a broader absorption profile. According to Park et al. [16], these two factors could help explain the synergistic effect observed when these molecules are combined in the same resin system. In the present study, both photoinitiators showed similar molar extinction coefficient values at their respective absorption peaks ($\varepsilon_{(468\ nm)}$ for CQ and $\varepsilon_{(392\ nm)}$ for PPD), but CQ presented higher levels of PD_{abs} than PPD when using the VIP as the LCU (Table 2). The LCU used in all experiments was a QTH type, with broad emission spectra, including the wavelength at which PPD is excited. Even still, CQ presented higher PD_{abs} compared to PPD and this can be explained by the lower spectral irradiance at 392 nm, where PPD has its absorption peak. The output from the quartz-tungsten-halogen light is a better match with CQ than with PPD.

Overall, for a given photoinitiator concentration, both DSC and FTIR showed that the photosensitive molecule used did not affect DC, in spite of the differences in the PD_{abs}. Thus, one can suggest that sufficient light energy was applied such that at these concentrations, each photoinitiator was operating at near maximum efficiency for this particular resin system. However, as far as R_p^{max} was concerned, statistically different values were obtained by each photoinitiator system and consistently ranked as CQ > CQ/PPD > PPD. This behavior is partially due to the fact that the VIP LCU had a less favorable spectral irradiance for PPD than CQ. This was true although CQ and CQ/PPD exhibited similar PD_{abs}. This can be explained, as previously mentioned, by the photochemistry of each photoinitiator. Although it seems that the major mechanism of free radical formation by the photolysis of PPD is the cleavage of the C-C bond between the two carbonyls [16, 21], the possibility that PPD reacts with a co-initiator has also to be considered [19]. However, based on the lower R_p^{max} observed in this study for the groups where CQ was not present, it can be speculated that the interaction between CQ and EDMAB was more efficient than that resulting from PPD [21]. A recently published study [34] demonstrated that the polymerization initiated by PPD progressed at a slower rate and exhibited lower DC than that initiated by CQ, even When the photon absorption efficiency for PPD was 40% higher than that for CQ, thus corroborating the results of the present study. More researches need to be carried out in order to determine the influence of the amine/photosensitive molecule ratio and to understand the actual interactions between the co-initiators.

The conversion curves obtained by DSC (Figure 2) also revealed that R_p^{max} occurred earlier in time with the increase of CQ concentration, which was not observed for the PPD and the combination CQ/PPD. One possible explanation for this fact is that PPD systems could be less reactive as a result of a less effective interaction with the co-initiator. On the other hand, the point in conversion where R_p^{max} happened was around 15% for all systems, with the exception of PPD at low concentration. This behavior is known as the “Trommsdorff effect”, “Trommsdorff-Norrish effect” or, simply, “gel effect” [8, 25]. At approximatley 15% of conversion for this resin system, the polymer experiences a sudden increase in viscosity, which impairs mobility and leads to a rapid decrease in the termination rate constant. Therefore, as the reaction becomes diffusion controlled, it relies on chain propagation to go forward [35]. For the PPD formulation at low concentration, the R_p^{max} occurred over a range of conversions, causing the R_P^{max} curve to plateau (Figure 2b). This behavior might offer some insight for explaining the lack of differences in DC among the photoinitiator types. While R_p^{max} for CQ peaked and dropped off dramatically, that of PPD, although being low, remained constant for about 4 s before dropping.

Although the degree of conversion assessed both by DSC and FTIR did not show differences among the photoinitiator types, composites formulated with PPD showed a trend toward the lowest KHN. Moreover, KHN values were statistically different among all levels of photoinitiator concentrations for the systems that presented the lowest R_p (PPD and CQ/PPD), unlike the CQ only groups, in which KHN values remained unchanged above the intermediate concentration. It previously has been suggested that the microhardness would be sensitive to even small changes in conversion that otherwise do not show statistical difference [30]. This may be due to the fact that the hardness measurements consider the overall sample structure (as involves plastic deformation), while the FTIR readings were performed with 150 µm chips from the surface. It can also be speculated that, even though the final DC was the same, the polymer structure might have been affected by the rate of polymerization. In fact, it was observed that groups that contained PPD only showed the lowest reaction rate at every concentration and also produced the lowest KHN values.

Whether rate of polymerization is correlated to network crosslinking is a matter of controversy in the literature [27-29]. It has been argued that if the point in conversion where R_p^{max} is achieved is low (as observed for the PPD groups), this is an indication that the reaction is prematurely deccelerating [36, 37]. However, this was expected to have been accompanied by lower conversion, which was not the case in the present study. This may point to the hypothesis that post-cure conversion for PPD groups is greater, as well as the aforementioned behavior of R_p^{max} remaining constant during a certain period of time.

Although a less crosslinked structure may be a liability, the fact that the reaction rate was lower for PPD or CQ/PPD groups may be an advantage from the standpoint of polymerization stress development [22, 23]. There is evidence that reducing the R_p will cause the polymerization stress to decrease [38], while maintaining adequate mechanical properties and low susceptibility to degradation in organic solvents [39]. However, as mentioned previously, this is a matter of controversy [27-29]. While there are no studies evaluating polymerization stress development with the use of alternative photoinitiators, preliminary tests by us have shown promising results.

The color measurements revealed that for all systems, the increase in the photoinitiator concentration was responsible for the higher b-values. Since all specimens were photoactivated at the same radiant exposure, this may indicate that unreacted species were present in the material. Other than produce the undesired yellowing effect, excess photoinitiator and products of their photolysis may leach out from the material into the saliva, with possible cytotoxic effects [12, 40].

PPD produced lower b-value compared to the CQ or CQ/PPD systems, but only in the low concentration group. Although this may be an advantage in terms of color, this groups exhibited the lowest mechanical properties. Also, as the concentration increased, CQ presented lower b-values than PPD and CQ/PPD, indicating that its photobleaching ability is greater compared to that of the PPD molecule. Though it was not the aim of the present study to establish a relationship between PD_{abs} and photobleaching ability, it could be stated that the CQ photobleaches more than PPD due to the higher PD_{abs}. However, the present data do not agree with this hypothesis, since CQ alone and the combination CQ/PPD showed similar PD_{abs} with different photobleaching behavior. Thus, it is possible that the interaction between the photosensitive molecule and the co-initiator is the key. Consequently, it can be hypothesized that CQ presented a better interaction with EDMAB in addition to presenting a higher PD_{abs}, as observed in this study.

5. CONCLUSION

The first hypothesis was partially accepted. PPD and CQ/PPD were able to promote similar DC compared to that resulting from CQ only, and with lower R_p. The use of PPD by itself resulted in lower KHN values and the yellowing reduction was only observed when PPD was used at low concentration, providing evidence that alternative photoinitiators might be used, but with care.

The second hypothesis was accepted. The correlation tests showed that the higher the PD_{abs} the higher was the DC, R_p^{max} and KHN. However, it seems that other variables, such as the reaction kinetics *per se* and the photoinitiator interaction with the co-initiator (as part of the photochemistry process), also play an important role.

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Table 1: Photoinitiator (Pt)/co-initiator (C) concentrations (in wt%) used in the present study.*

	Concentration					
	Low		**Intermediate**		**High**	
	Pt (wt%)	**C (wt%)**	**Pt (wt%)**	**C (wt%)**	**Pt (wt%)**	**C (wt%)**
CQ	0.33	0.17	0.66	0.34	1	0.5
PPD	0.33	0.17	0.66	0.34	1	0.5
CQ/PPD	0.17/ 0.17	0.17	0.34/ 0.34	0.34	0.5/ 0.5	0.5

*Concentration based on the total matrix resin weight. Note that the photoinitiator/amine ratio was kept constant (2:1) for all of the mixtures.

Table 2: Molar extinction coefficients of the photoinitiators and absorbed power density from the VIP light curing unit.

Photoinitiator	Concentraton	$\varepsilon_{(\lambda)}$ (mm^{-1} mol^{-1L})*	PD$_{abs}$ (mW/cm^3)
CQ	**Low**	40.4	266
	Intermediate		517
	High		810
PPD	**Low**	37.3	197
	Intermediate		374
	High		601
CQ/PPD	**Low**	Not tested	253
	Intermediate		497
	High		800

*Molar extinction coefficient at the photoinitiators' respective absorption peaks: $\varepsilon_{(468\ nm)}$ for CQ and $\varepsilon_{(392\ nm)}$ for PPD.

Table 3: Results obtained for the variables tested: degree of conversion (DC) and maximum rate of polymerization (R_p^{max}) by the DSC method, Knoop hardness (KHN), DC by the FTIR method and b-value ("yellowing effect").*

Variable	Photoinitiator	Concentration		
		Low	Intermediate	High
DC (%) - by the DSC	CQ	62.19 (1.29) ^{Aa}	62.81 (0.74) ^{Aa}	65.13 (0.69) ^{Aa}
	PPD	56.76 (3.36) ^{Ba}	66.24 (4.73) ^{Aa}	67.77 (5.27) ^{Aa}
	CQ/PPD	60.52 (1.49) ^{Ba}	69.15 (6.01) ^{Aa}	68.97 (0.80) ^{Aa}
R_p^{max} (%/sec) - by the DSC	CQ	3.1 (0.0) ^{Ca}	4.6 (0.1) ^{Ba}	5.2 (0.1) ^{Aa}
	PPD	1.7 (0.1) ^{Cc}	3.0 (0.1) ^{Bc}	3.8 (0.2) ^{Ac}
	CQ/PPD	2.1 (0.1) ^{Cb}	3.5 (0.1) ^{Bb}	4.6 (0.2) ^{Ab}
KHN (kgf/mm^2)	CQ	27.67 (0.75) ^{Ba}	36.66 (1.36) ^{Aa}	37.89 (0.79) ^{Aa}
	PPD	24.50 (2.08) ^{Cb}	30.30 (0.83) ^{Bc}	34.73 (1.37) ^{Ab}
	CQ/PPD	25.58 (0.11) ^{Cb}	32.59 (0.38) ^{Bb}	38.65 (1.01) ^{Aa}
DC (%) - by the FTIR	CQ	65.53 (2.50) ^{Ba}	73.50 (2.12) ^{Aa}	76.23 (1.72) ^{Aa}
	PPD	67.14 (2.34) ^{Ba}	72.28 (3.06) ^{Aa}	72.18 (1.90) ^{Aa}
	CQ/PPD	62.4 (0.92) ^{Ca}	71.11 (0.39) ^{Ba}	75.16 (1.91) ^{Aa}
Yellowing (b-value)	CQ	+ 1.5 (0.2) ^{Ca}	+ 4.3 (0.1) ^{Bb}	+ 7.1 (0.6) ^{Ac}
	PPD	+ 0.7 (0.2) ^{Cb}	+ 4.9 (0.2) ^{Ba}	+ 10.0 (0.7) ^{Aa}
	CQ/PPD	+ 1.7 (0.1) ^{Ca}	+ 4.0 (0.2) ^{Bb}	+ 8.1 (0.2) ^{Ab}

**Values followed by the same lower case letter in the same column or by the same upper case letter in the same row are statistically equivalent ($p<0.05$) according the Tukey's test. P-values according the two-way ANOVA: DC (DSC): photoinitiator type (Pt) = 0.170, concentration (C) = <0.001 and interaction between Pt and C (Pt*C) = 0.162. R_p^{max}: Pt = <0.001, C = <0.001 and Pt*C = 0.026. KHN: Pt = <0.001, C = <0.001 and Pt*C = <0.001. FTIR: Pt = 0.097, C = <0.001 and Pt*C = 0.050. Yellowing: Pt = <0.001, C = <0.001 and Pt*C = <0.001.*

Figure 1: Spectral irradiance of the light curing unit (measured irradiance = 514 mW/cm^2) (A) and light absorption spectra of the different photoinitiator systems (B).

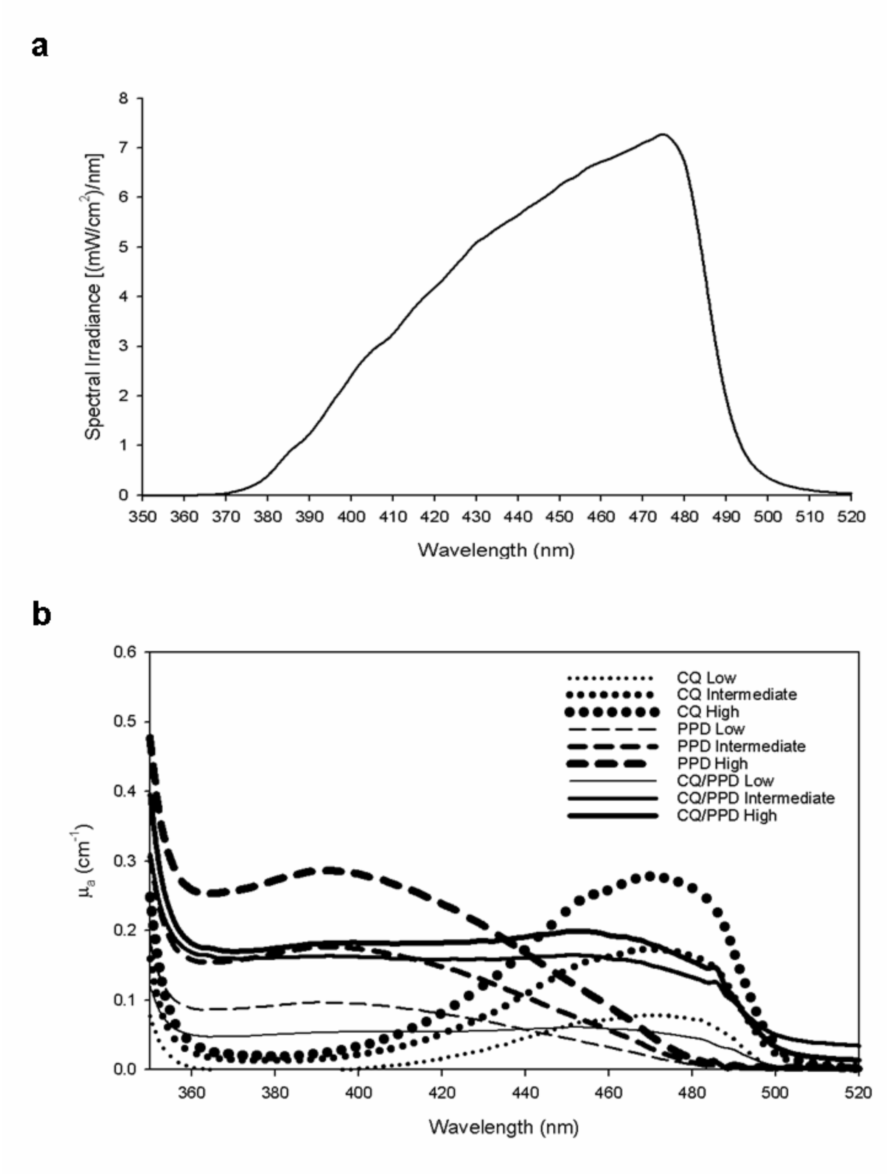
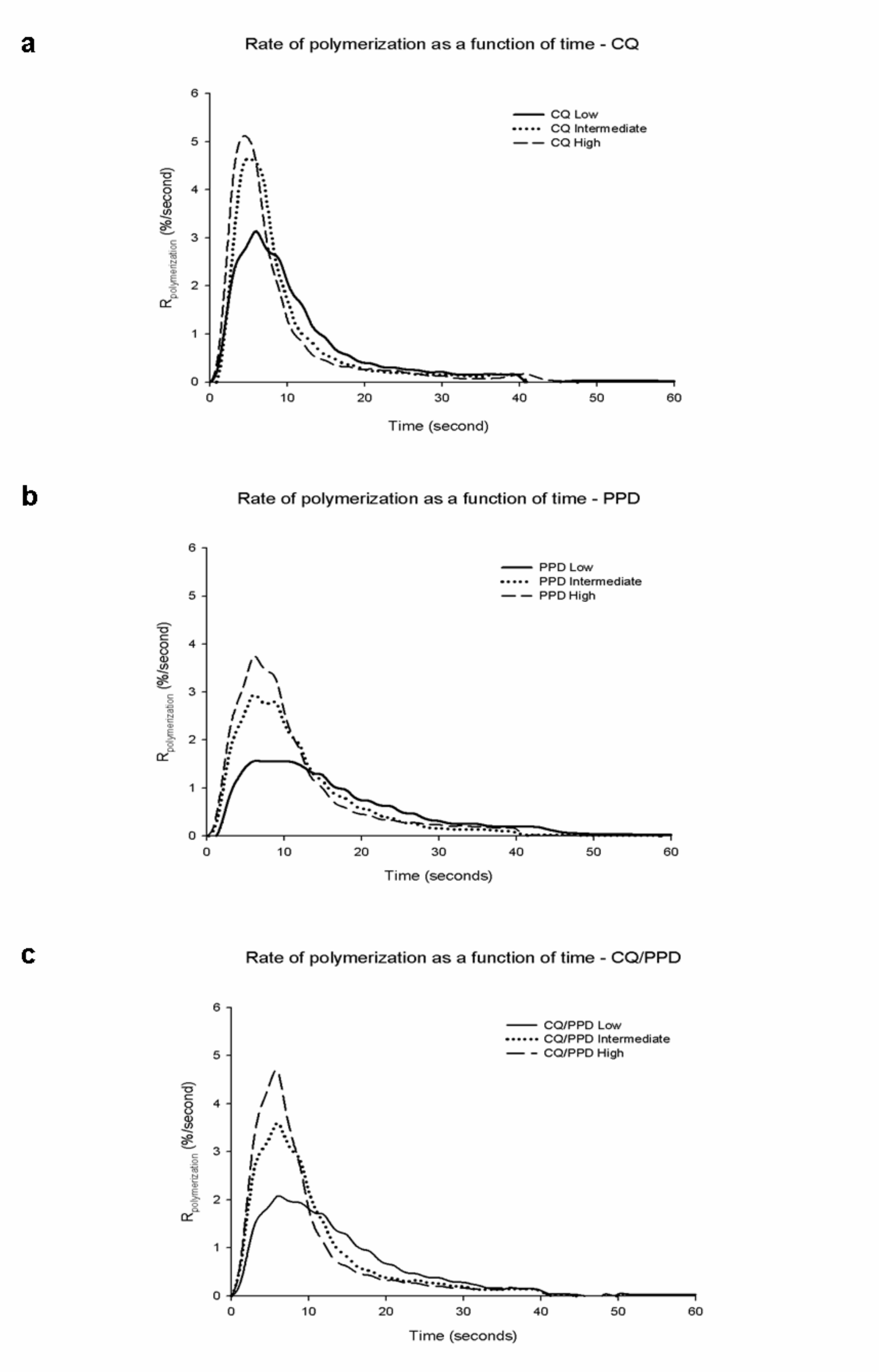


Figure 2: Rate of polymerization curves obtained by the photo-DSC.



CAPÍTULO 2

EFFECT OF CO-INITIATOR RATIO ON THE POLYMER PROPERTIES OF EXPERIMENTAL RESIN COMPOSITES FORMULATED WITH CAMPHORQUINONE AND PHENYL-PROPANEDIONE.

ABSTRACT

Objectives: To evaluate the effect of amine ratio (ethyl 4-dimethylaminobenzoate, EDMAB) on the maximum rate of polymerization (R_p^{max}), degree of conversion (DC), Knoop hardness (KH), water sorption (Wsp), water solubility (Wsl) and color changes (ΔE) over time of resin composites formulated with the photoinitiators camphorquinone (CQ), phenylpropanedione (PPD) and CQ-PPD in combination. **Materials and methods:** Experimental resin composites were made with photoinitiator:amine ratios of 2:1, 1:1, 1:1.5 and 1:2 by weight. R_p^{max} was evaluated with differential scanning calorimetry (DSC), DC with DSC and Fourier Transformed Infrared Spectroscopy (FTIR), KH with Knoop indentation, Wsp and Wsl adapted from ISO 4049; and color with a chromameter. The results were analyzed with two-way ANOVA/Tukey's multiple comparison test ($p<0.05$). **Results:** The higher the amine ratio in the composite, the higher was DC, R_p^{max}, and KH, and the lower was Wsl, regardless of the photoinitiator type. The use of PPD alone resulted in poorer properties than CQ and CQ-PPD. Many factors seem to affect the color changes and the b-axis data revealed that the higher the amine ratio, the higher was the +b value (yellowing) for CQ and CQ-PPD formulations. **Conclusions:** The use of PPD alone was not advantageous for producing good final properties when compared to CQ and CQ-PPD. The photoinitiator efficiency was dependent on the amine

ratio, regardless of the amine type. The amine ratio strongly affected the yellowing for resin composites with CQ and CQ-PPD.

INTRODUCTION

The combination of camphorquinone (CQ) and amine has been widely used as a photoinitiator/co-initiator system since the introduction of visible-light activated resin composites [1, 2]. Basically, the absorption of light by CQ raises the molecule to an excited state, known as the “triplet-state”, with very short half-life [3]. If the excited CQ interacts with an amine molecule, it results in an excited state complex, called “exciplex” [4]. In this state, CQ can abstract a hydrogen atom from the tertiary amine, resulting in the formation of a free radical [5]. Thus, factors like the CQ and amine concentrations, their ratio, the molecular structure of the amine, and the reactivity of the formed radicals to initiate monomer polymerization, all play important roles in the polymerization reaction and, consequently, on the properties of the resultant polymer [6-10].

The generation of free-radicals is directly dependent on the ratio of CQ and amine, as well as the type of amine. Some amines can actually be used as polymerization inhibitors. The behavior seems to be dependent on many factors, such as the number of methyl groups attached to the nitrogen atom as well as the potential for steric hindrance [5]. In any case, above certain limits, any amine co-initiator may act as a retarder [5, 6, 10] because an excess of amine may quench the triplet state of CQ and/or trap initiating radicals by termination reactions [8]. An additional problem is that an excess of amine can cause color instability because of the eventual formation of oxidative products [11,12].

Since the intense yellow hue of CQ may also affect resin esthetics, alternative photoinitiators have been studied [13-16]. Phenyl-propanedione (PPD) was suggested as a photoinitiator for application in dental composites in 1999 by Park et al [13]. According to these authors, this molecule could generate free radicals by photo-cleavage and proton abstraction, but the former would prevail. Consequently, there may be less need for a co-initiator. As the system is not dependent on amines, it could be suggested that the darkening effect caused by oxidation products from these compounds could also be avoided. However, recent studies have speculated that the performance of PPD may also be dependent on its use with an amine, and its type and concentration [17-19].

As described above, there are many uncertainties concerning the effects of the co-initiator ratio on the polymerization reaction and properties of resin composites formulated with different photoinitiators. Therefore, the aims of the current study were: a) to evaluate the influence of the amine ratio on the maximum rate of polymerization (R_p^{max}), degree of conversion (DC), Knoop hardness (KH), water sorption (Wsp) and water solubility (Wsl) of resin composites formulated with CQ, PPD and CQ-PPD in combination; and b) to describe the color changes (ΔE) in these materials over time, with special consideration to the degree of yellowing.

The hypotheses tested were that:

i) the efficiency of CQ, but not PPD, is related to the photoinitiator/amine ratio (i.e. increasing the amount of amine improves material properties for CQ, but not for PPD);

ii) for PPD formulations, since the photoinitiator does not interact with the co-initiator, a higher amine ratio will lead to more yellowing because the amine is not used up in the reaction;

iii) for CQ formulations, the degree of yellowing in the first 24 hours would be less for samples with higher amine ratios due to the higher amount of photoinitiators consumed. However, after water storage, the higher the amount of amine, the higher the degree of yellowing due to the increased formation of oxidation products.

MATERIALS AND METHODS

1. Materials tested

The monomers 2,2 bis[4-2(2-hydroxy-3-methacroyloxypropoxy)phenyl] propane (Bis-GMA, Esstech, Essington, PA, USA) and triethyleneglycol dimethacrylate (TEGDMA, Esstech) were mixed in equal parts by weight. Camphorquinone (CQ, Polysciences Inc., Warrington, PA, USA) or 1-phenyl-1,2- propanedione (PPD, Aldrich Chem. Co., Milwaukee, WI, USA) were used as photoinitiators. The tertiary amine, ethyl 4-dimethylaminobenzoate (EDMAB, Avocado, Heysham, Lanchire, UK), was used as a co-initiator. The photoinitiator:amine ratios tested were: 2:1 (0.3:0.15 wt%), 1:1 (0.3:0.3 wt%), 1:1.5 (0.3:0.45 wt%) and 1:2 (0.3:0.6 wt%). The combination of both photoinitiators (CQ-PPD) was also tested in equal parts by weight (0.15 wt% of each photoinitiator). 2,6-di-*tert*-butyl-4-methyl-phenol (BHT, Aldrich) was added to each formulation at 0.05 wt% as an inhibitor. Silane treated glass fillers (strontium glass with 2-3 μm average size and fumed silica of 40 nm average size, in a 15:1 ratio by weight) were added at 60 total wt%. All the components were homogeneously mixed (DAC 150 Speed Mixer, Flacktek, Landrum, SC, USA) for 1 minute at 1300 rpm. All materials were prepared and handled under safe yellow light. All photoactivation procedures were carried out with a quartz-tungsten-halogen (QTH) lamp (VIP, Bisco Inc., Schaumburg, IL, USA).

2. Differential scanning calorimetry (DSC)

Real-time polymerization was assessed by differential scanning calorimetry (DSC). Ten milligrams of composite (approximately 130 μm thick) was photoactivated in standard aluminum pans (Perkin-Elmer Inc., Wellesley, MA, USA) in the DSC chamber (DSC 7, Perkin-Elmer Inc., Wellesley, MA, USA) under nitrogen gas purge (20 psi) at 25°C (n=3). Each specimen was irradiated in the DSC three times. Each DSC thermogram comprised 40 second of irradiance at 235 mW/cm^2. The peak in the first thermogram represented the exotherm generated by the polymerization of the material plus the heat generated by the light curing unit. The peaks in the next two thermograms represented only the heat generated by the light curing unit on the polymerized material (the second two thermograms were essentially equivalent and lower than the first). The area under each heat flow peak was integrated. The isothermal heat of reaction was obtained by subtracting the average of the peak areas in the last two thermograms from the area of the first peak. Real-time degree of conversion (DC) was calculated by dividing the cumulative heat flow (registered at one data point per second) with the theoretical heat release per mole of reacted carbon double bonds (56 kJ/mol). The maximum rate of conversion (R_p^{max}) was found by taking the first derivative of the DC with respect to time.

3. Fourier transformed infrared spectroscopy (FTIR)

Ten milligrams of resin composite was applied and light activated in standard aluminum pans in the DSC chamber under the same conditions as described above (n=3). However, specimens were photoactivated with a single 40 sec exposure. Small chips removed with a scalpel from the sample were placed on a KCl crystal for transmission FTIR (DS20/XAD microscope, Analect Instruments, Irvine, CA, USA) 24 hrs after storage at room temperature (25±1°C). Thirty scans were taken at 8 cm^{-1} resolution. Five measurements were made with chips removed from different regions of the sample and an average DC value was calculated. The paste of the uncured composite was similarly tested. DC was calculated from the ratio of the C=C peak from the methacrylate group to that of the unchanging C…C peak from the aromatic ring for the uncured and cured specimens using standard baseline techniques.

4. Knoop hardness

Specimens were made by placing the resin composite in a stainless steel mold (8.7 mm diameter and 1 mm thick) sandwiched between clear matrix strips (n=5). The composite was photoactivated for 40 sec at 514 mW/cm^2, directly though the Mylar in order to produce a more clinically relevant irradiance, which was not possible in the DSC set up. The specimens were stored dry in a dark container for 24 hours at room temperature (25±1°C). Measurements were taken with a 100 g load applied for 20 s (Kentron Hardness Tester, Torsion Balance Co., Clifton, NJ, USA). Five indentations per surface were averaged for each specimen on the irradiated surface.

5. Water sorption and solubility

Specimens were made by placing the resin composite in a stainless steel mold, 8.66 mm diameter and 0.60 mm thick, sandwiched between clear matrix strips (n=6). These measures were used to keep the same ratio as the ISO 4049 instructions, but with similar diameter as the light guide. The composite was photoactivated for 20 sec at 514 mW/cm^2 on each side.

Immediately after curing, the specimens were transferred to a desiccator maintained at 37 (+/- 1) °C. After 22 hrs, specimens were removed and store in a second desiccator maintained at 25 (+/- 1) °C for 2 hrs and weighed. This cycle was repeated until a constant mass, m_1, was obtained. After final drying, specimen measures were taken to calculate volume (V) in cubic millimeters. Therefore, the specimens were immersed in distillated water at 37 (1) °C for 30 days. After this period, the resin composite discs were removed and washed with water. The excess water was removed by blotting with a tissue and the specimens were re-weighed (m_2). After this weighing, the specimens were reconditioned to constant mass (m_3) in the desiccators using the cycle described above for m_1. The following calculations were applied to obtain Wsp and Wsl in micrograms per cubic millimeter: Wsp = $(m_2 - m_3)/ V$ and Wsl = $(m_1 - m_3)/ V$.

6. Color change

The resin composite was photoactivated for 40 sec at 514 mW/cm^2 inside a stainless steel mold (8.7 mm diameter and 1 mm thickness) sandwiched between clear matrix strips (n=3). A chromameter (CR-221, Minolta Corp., Ramsey, NJ, USA) was used to check the CIELab parameter, that is composed of 3 axes: L (lightness, from

0=black up to 100=white), a (from –a=green up to +a=red) and b (from –b=blue up to +b=yellow). The color changes (ΔE) were calculated by the following formula: $\Delta E = [(\Delta L)^2 + (\Delta a)^2 + (\Delta b)^2]^{1/2}$.

Readings were performed immediately after the photoactivation procedure and repeated after 90 minutes and 24 hrs storage at room temperature (25±1°C) under dry conditions. Subsequently, the samples were immersed in distilled water at room temperature and readings were performed 7 days, 14 days, one month and two months (considering the photoactivation procedure as the initial time).

7. Statistical analyses

The results for each test were analyzed by use of two-way ANOVA (photoinitiator type and amine ratio) followed by Tukey's multiple comparisons test ($\alpha \leq 0.05$).

RESULTS

Table 1 shows the mean values of DC, R_p^{max}, KH, Wsp and Wsl. With the exception of Wsp, the results for each property were dependent upon the photoinitiator type and the ratio of photoinitiator and amine.

Figure 1 shows the ΔE values over time for all the materials tested. For CQ and CQ-PPD formulations, the value increased until seven days after photoactivation, and then the values tended to stabilize and/or decrease (Figure 1a and 1c). In general, the higher the amine content, the higher the ΔE. For the PPD formulations, there was a sharp increase in ΔE after 24 hours, and after the water immersion, a sharp decrease to a constant level was observed, regardless of the amine ratio (Figure 1b).

The *L* values over time are shown in Figure 2. For CQ and CQ-PPD, the values seem to increase up to about 7 days for materials with the lowest amine content (photoinitiator:amine ratio 2:1), while being relatively stable for all others. For the PPD formulations, there was an abrupt change during the 24 hrs dry storage with a subsequent decrease to a constant level after water immersion. The lower the amine content, the higher were the *L* values.

Figure 3 shows the *a* values over time. There was a clear trend to shift to green (negative values) over time for all the formulations for the first 24 hours or 7 days. After this, the values either stabilized or showed a slight recovery.

All formulations showed an increase in yellowing (+b) during the first 24 hours or 7 days (Figure 4). This increase was more pronounced for the CQ and CQ-PPD formulations, especially during the dry storage period of the first 24 hours. Higher +*b* values were associated with higher amine content. After water immersion, the materials containing less amine (2:1 and 1:1) demonstrated a subsequent stabilization, while those containing higher amine ratios (1:1.5 and 1:2) showed reduced yellowing. For the PPD formulations, the amine ratio did not seem to have an influence on yellowing.

DISCUSSION

Though the basic mechanism of interaction between CQ and amines has been established, many significant questions remain unsolved [5, 9]. Furthermore, studies that address the effect of co-initiator additions to mixtures formulated with PPD are scarce and the results are often contradictory [14, 16, 18, 19]. Thus, the present study proposed a systematic evaluation of the influence of the amine ratio on the reaction kinetics and the final properties of resin composites formulated with CQ, PPD or CQ-PPD. Three hypotheses were tested and all of them were rejected.

Though CQ itself can initiate polymerization, amines are used as co-initiators to accelerate the reaction through the formation of aminoalkyl radicals [4]. Since the efficiency of this process depends on the steric structure of these radicals [9], it is important to consider the amine type used. The present investigation used the molecule EDMAB, because of its well known reactivity with CQ [20]. The present investigation demonstrated that when the amount of EDMAB was increased, the R_p^{max}, DC and KHN for resin composites containing CQ (CQ alone and CQ-PPD) also was increased. These results agree with those of previous researchers that state that the efficiency of radical generation has a direct influence on the efficiency of polymerization [8, 10].

It was assumed that the mechanism of free radical generation by the photolysis of PPD is the cleavage of the C-C bond between the two carbonyls [14]. This assumption was based on the results of a previous study that showed that the photodecomposition rate of CQ increased with the addition of amine (*N,N*-dimethylaminoethyl methacrylate – DAEM), while that of PPD decreased [16]. Indeed, Newmann et al. [16] hypothesized that PPD could also react via a co-initiator, as it bears the same diketone group as CQ. They also presented experiments in which methyl-methacrylate was photopolymerized in the presence of PPD with and without the addition of the co-initiator ethyl p-dimethylamino benzoate, and showed similar reaction rates in both cases. Consequently, this indicated to the authors that the second mechanism of radical generation for PPD does not exist.

The results from the aforementioned studies indicate that the PPD reaction would not be dependent on the presence of amines. However, the outcomes of this study suggest the opposite. The ANOVA revealed that DC, KHN, R_p^{max} and Wsl were dependent on the amine ratio, indicating that PPD efficiency is also related to the amine content and that hydrogen abstraction might have an important role, other than PPD cleavage by itself. It also is important to note that in a pilot study for this project, it was not possible to polymerize formulations containing PPD without amine using 40 seconds of light exposure. These results agree with recent published studies in which the presence of amines markedly enhanced the efficiency of PPD, and also demonstrates that hydrogen abstraction is the dominant decomposition mechanism for this molecule [18, 19]. Thus, the first hypothesis was rejected since the efficiency of both photoinitiators was related to the amine ratio.

The best results achieved with CQ and CQ-PPD resulted in polymers with higher DC, R_p^{max}, KHN and lower Wsl than the best ones achieved with PPD only. It could be assumed that the different behavior between CQ and PPD molecules might be related to the better correlation between CQ and the QTH absorption and emission spectra, respectively, known in the literature as the “integrated relative curing potential” [21] or the “photon absorption efficiency” (PAE) [15]. However, a very recent publication demonstrated that the polymerization initiated by PPD progressed at a slower rate and exhibited lower DC than that with CQ, even in a situation where the PAE for PPD was 40% higher than for CQ [18]. Therefore, the authors’ assumption that the lower efficiency of PPD compared with CQ cannot be attributed to an inefficient overlap between the PPD and the light curing unit spectra, but to a lower efficiency of PPD, are in agreement with the outcomes of the current study. As the efficiency of polymerization depends on the structure of each specific amine and the reactivity of the corresponding amine-derived radicals toward the initiation of the acrylic monomer polymerization [10], additional studies are necessary to understand the influence of the amine structure on the process of generating free radicals by the PPD photoinitiator.

Regardless of the photoinitiator type used, the amine ratio did not affect the Wsp. This might be related to the fact that water sorption seems to be more dependent on the monomers used than the final DC [22]. In contrast, lower solubility in water was recorded for formulations containing higher amine ratios. It is interesting that for a given photoinitiator type, formulations exhibiting similar DC, but different Rp, exhibited different Wsl. It has been hypothesized that the polymer crosslink density is affected by the speed of reaction [23], and this may affect solubility, it has also to be considered that formulations exhibiting similar R_p^{max}, but different DC (for example, CQ:amine 2:1 and CQ-PPD:amine 1:2), also demonstrated different solubility in water. Therefore, solubility may be affected both by the extent of cure of the network polymer, as well as its cross-linked structure.

The ΔE value changes over time are probably related to various phenomena for the different photoinitiator types tested, though a sharp increase followed by decrease and/or stabilization occurred for all the tested groups. For the resin composites formulated with PPD only, the *L* value seems to guide the changes. The sharp increase in the dry storage period (24 hrs) can be explained by the changes in the light scattering and absorption properties, including light reflectivity and translucency [24]. The reduction in the L value after water immersion is probably due to the penetration of water through the resin matrix, which also alters the scattering pattern leading to a change in the opacity of the composite [25]. A possible relationship between lower DC and higher *L* value changes is also supported by the fact that composites with CQ and CQ-PPD demonstrated higher changes in L for the lower amine ratio (photoinitiator:amine 2:1).

While the *a* data seem not to be affected by the amine ratio and/or the photoinitiator type (with the exception of CQ-PPD:amine 2:1 which had a tendency for negative values that stabilized after water immersion), *b* was affected by both. Immediately after curing, the PPD and CQ-PPD samples exhibited lower yellowing than those with CQ, which was expected since the major absorption for PPD occurs at lower wavelengths than for CQ. Thus, the use of PPD might be considered advantageous in terms of esthetics. However, previous studies demonstrated that the benefits are dependent on the concentration [26]. Furthermore, after two months of water storage, the *b* values became very similar (with the exception of CQ:amine 1:2), which could be related to the leaching of the non-reacted CQ molecules into water.

The effect of amine ratio on the yellowing effect seems to be dependent on the photoinitiator type. For resin composites formulated with CQ (CQ alone and CQ-PPD), a greater yellowing effect was associated with the use of a higher amine ratio. This effect could be related to the excess of amine, since it is well known that amines have a great potential for darkening due to oxidative reactions [11], and excess amine that is left over after the reaction may induce yellowing in the resin. However, this effect was not seen for resin composites with PPD alone. Therefore, the second hypothesis was rejected. As the potential for creating free radicals by the interaction of PPD with EDMAB seems to be less than for CQ and EDMAB, it is possible that the oxidation of residual amine molecules is not the only cause for the yellowing in these resin composites during water storage

A hypothetical explanation could be related to the dependency on the photoinitiator consumption and the viscosity development during the polymerization. Maybe the higher amine ratios reduce the dependency on the CQ molecule to initiate the process and, consequently, higher amounts of non-consumed photoinitiator are present in these systems. Additionally, resin composites containing CQ (CQ alone and CQ-PPD) with higher amine ratios (1:1.5 and 1:2) achieve the gel point at early stages of the reaction (as demonstrated by the earlier reaction peak time) than those with lower amine contents. Thus, the viscosity of the system increases more quickly, which reduces the efficiency of photoinitiator diffusion. Consequently, the greater numbers of CQ molecules that return to the original state increase the +*b* value (yellowing) until the seventh day. However, due to the leaching of these unreacted molecules, the b values ultimately decreased over time. So, the third hypothesis was also rejected and more studies should be carried out in order to determine the leachable components from these materials and provide more conclusive explanations for these phenomena.

CONCLUSIONS

Though the use of PPD alone reduced the final properties of the composite, the present investigation demonstrated that the mixture of equal parts of CQ and PPD resulted in similar DC, KHN and Wsl to that in formulations having the same amount of

CQ alone. Additionally, the mixture CQ-PPD produced lower R_p^{max}, which might be advantageous for reducing the rate of polymerization stress development. This has been identified as a potential benefit from pilot studies performed with these mixtures. On the other hand, the substitution of CQ by PPD did not reduce the yellowing effect.

The best performances (DC, KHN and Wsl) were achieved with CQ:amine 1:1.5, CQ:amine 1:2, CQ-PPD:amine 1:1.5 and CQ-PPD:amine 1.2. It seems that the use of 1:2 ratio of CQ:amine has the greatest potential for producing yellowing in the resin matrix. This is likely due to oxidation reactions involving the excess of amine left in the composite.

The first hypothesis was partially rejected. The PPD performance was also dependent on the amine ratio.

The second hypothesis was rejected. The amine ratio did not influence the yellowing effect for formulations containing PPD alone.

The third hypothesis was rejected. The yellowing was higher for samples with higher amine ratios at the beginning, and stabilized after water storage.

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Table 1: Mean values (standard deviation) of degree of conversion (DC) by the DSC and FTIR, maximum rate of polymerization (R_p^{max}), Knoop hardness (KHN), water sorption and solubility.

Photoinitiator:coinitiator	DC by DSC, %	R_p^{max}, %/sec	DC by FTIR, %	KHN, kgf/mm²	Sorption, µg/mm³	Solubility, µg/mm³
1) CQ:amine 2:1 (control)	60.01 (1.28) **b**	2.80 (0.00) **c**	59.86 (1.96) **bc**	27.97 (1.42) **de**	29.32 (3.92) **a**	23.39 (4.15) **a**
2) CQ:amine 1:1	60.58 (0.89) **b**	3.73 (0.06) **b**	64.02 (2.66) **ab**	34.83 (0.29) **ab**	29.58 (1.30) **a**	11.00 (2.11) **c**
3) CQ:amine 1:1.5	61.91 (1.62) **ab**	3.86 (0.11) **b**	65.36 (2.55) **ab**	36.53 (1.33) **a**	29.74 (4.26) **a**	6.78 (1.39) **d**
4) CQ:amine 1:2	62.24 (0.87) **ab**	4.03 (0.06) **a**	65.23 (2.23) **a**	38.60 (3.06) **a**	33.97 (5.44) **a**	4.32 (1.95) **d**
5) PPD:amine 2:1	56.61 (1.40) **c**	1.73 (0.06) **h**	53.07 (0.91) **d**	27.16 (1.00) **e**	31.61 (3.26) **a**	23.24 (2.69) **a**
6) PPD:amine 1:1	56.44 (1.20) **c**	1.83 (0.06) **g**	51.11 (0.63) **d**	25.30 (0.82) **e**	30.61 (2.40) **a**	16.80 (2.86) **b**
7) PPD:amine 1:1.5	58.43 (1.26) **bc**	2.13 (0.06) **f**	51.44 (0.78) **d**	32.17 (2.90) **bc**	30.12 (3.66) **a**	9.64 (4.55) **c**
8) PPD:amine 1:2	59.02 (1.75) **bc**	2.33 (0.06) **e**	55.94 (0.68) **cd**	31.83 (0.42) **bc**	28.10 (1.84) **a**	11.16 (3.42) **c**
9) CQ-PPD:amine 2:1	57.85 (1.25) **bc**	1.83 (0.11) **g**	51.95 (4.02) **d**	25.07 (2.18) **e**	31.37 (2.40) **a**	27.37 (2.08) **a**
10) CQ-PPD:amine 1:1	59.97 (0.49) **b**	2.47 (0.06) **d**	55.37 (2.47) **cd**	30.70 (0.62) **cd**	30.50 (4.28) **a**	11.58 (2.39) **c**
11) CQ-PPD:amine 1:1.5	63.49 (0.87) **ab**	2.80 (0.00) **c**	61.24 (2.10) **ab**	36.60 (1.65) **a**	30.71 (1.98) **a**	7.43 (2.95) **cd**
12) CQ-PPD:amine 1:2	64.23 (2.07) **a**	2.83(0.06) **c**	59.57 (4.54) **abc**	34.60 (0.63) **ab**	28.93 (2.51) **a**	6.24 (2.22) **d**

Values followed by the same lower case letter in the same column are statistically equivalent ($p<0.05$) according the Tukey's test.

P-values according the two-way ANOVA: DC (DSC): photoinitiator type (Pt) = 0.000, amine ratio (AR) = 0.000 and interaction between Pt and AR (Pt*AR) = 0.012 / R_p^{max}: Pt = 0.000, AR = 0.000 and Pt*AR = 0.000/ DC (FTIR): Pt = 0.000, AR = 0.000 and Pt*AR = 0.030 / KHN: Pt = 0.000, AR = 0.000 and Pt*AR = 0.001/ Sorption: Pt = 0.859, AR = 0.947 and Pt*AR = 0.091/ Solubility: Pt = 0.000, AR = 0.000 and Pt*AR = 0.002.

Figure 1: ΔE values over time for all the materials tested.

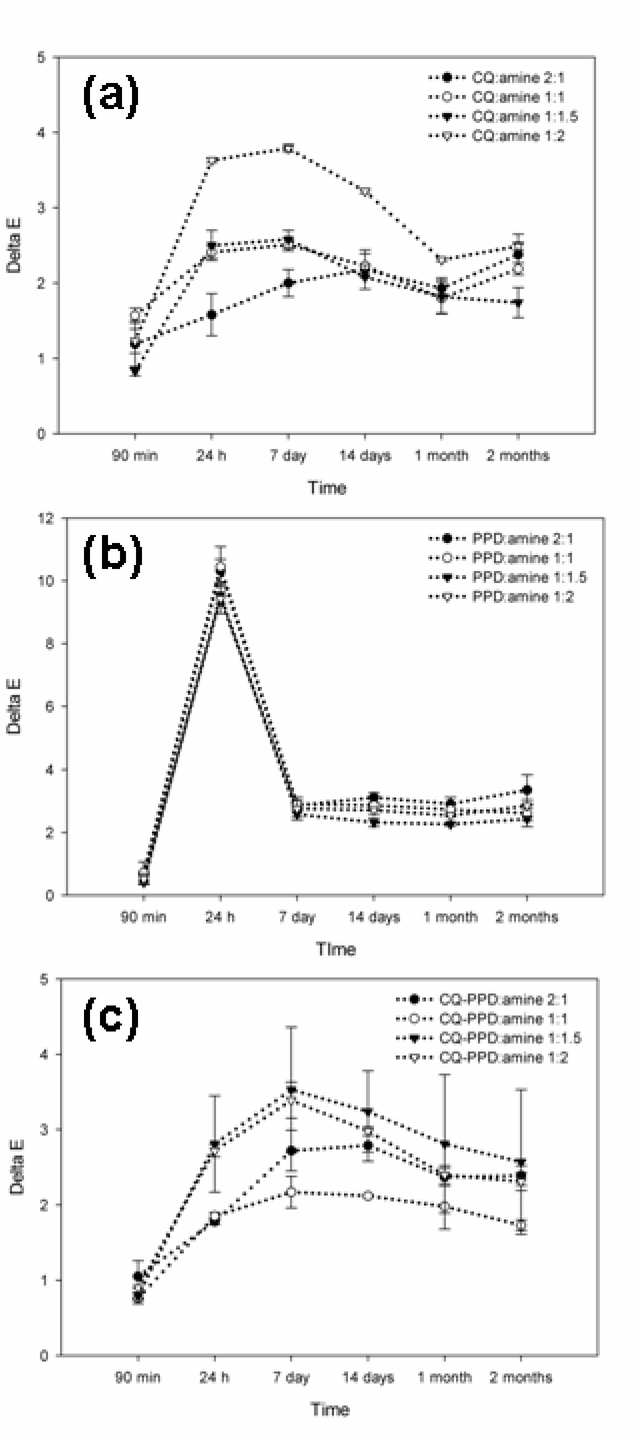


Figure 2: *L* values over time for all the materials tested.

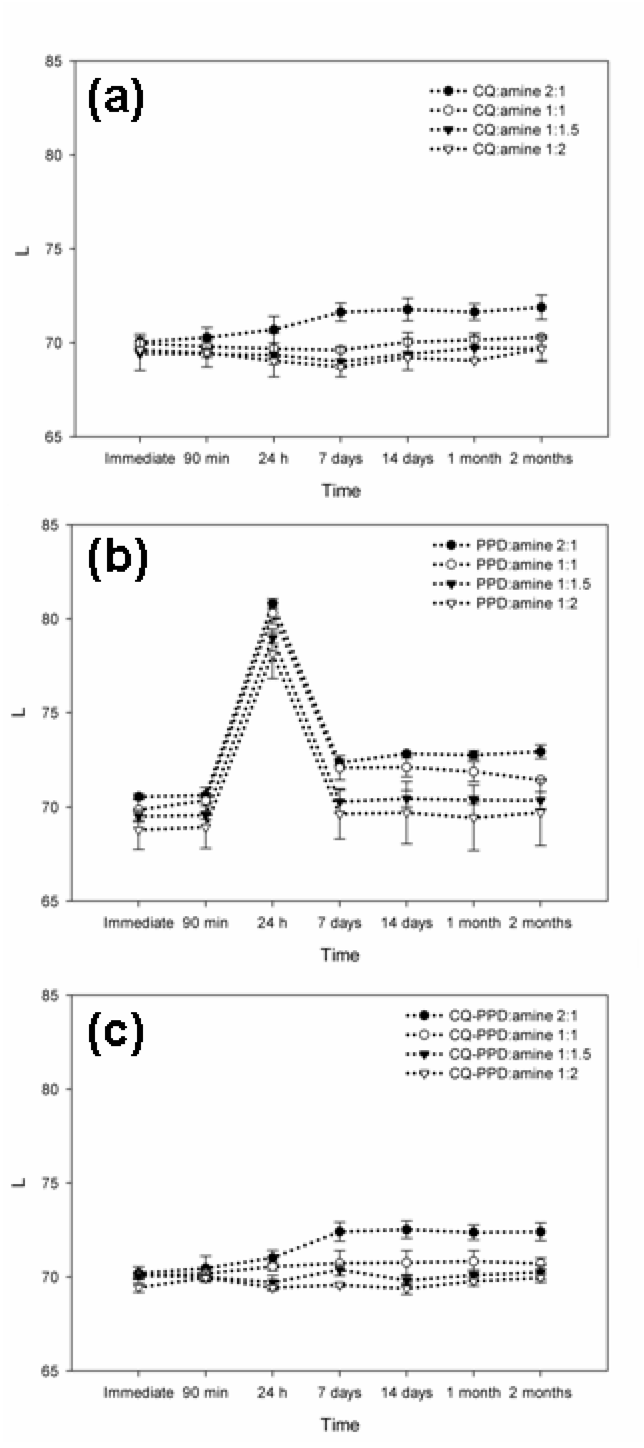


Figure 3: *a* values over time for all the materials tested.

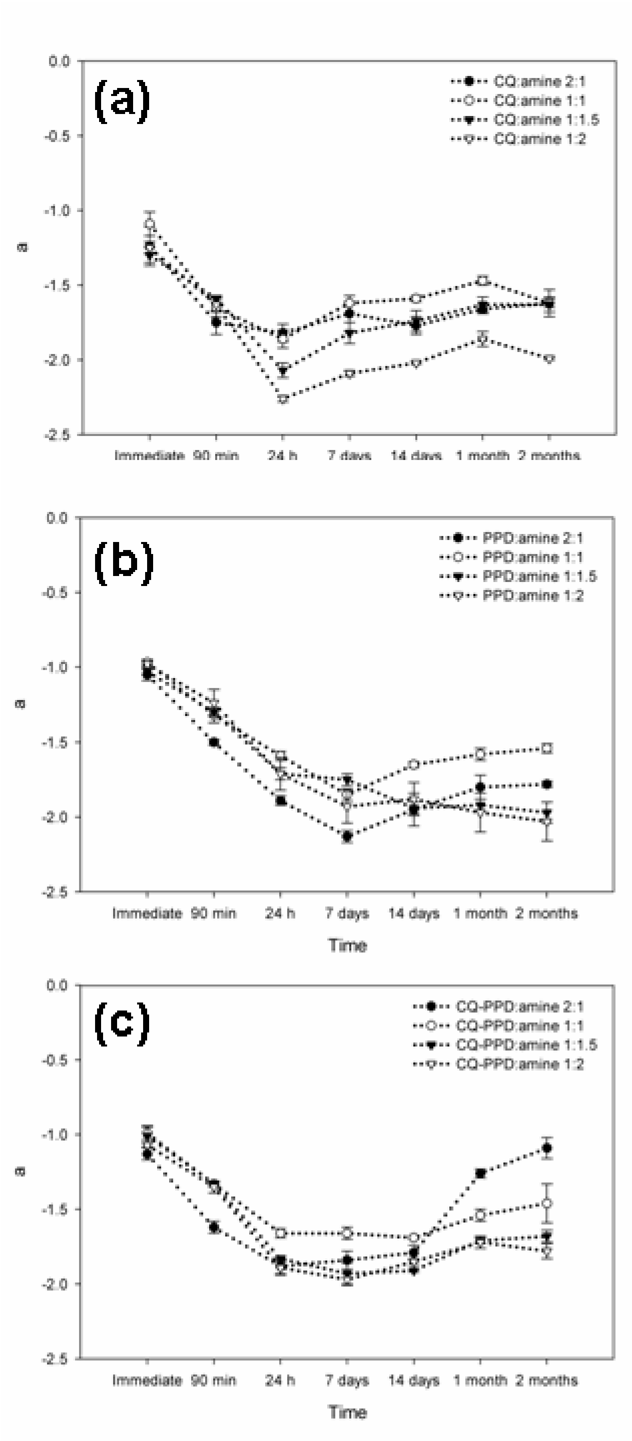
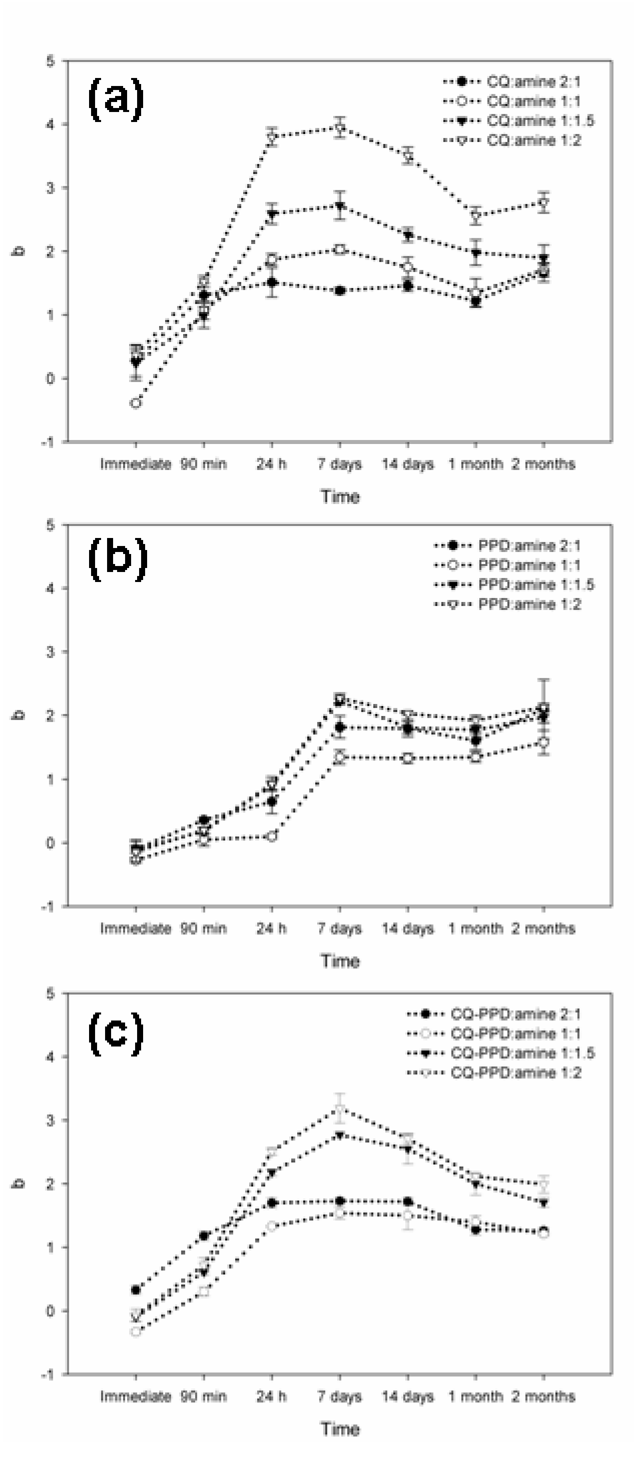


Figure 4: ***b*** values over time for all the materials tested.



CAPÍTULO 3

ALTERNATIVE PHOTOINITIATOR SYSTEM REDUCES THE RATE OF STRESS DEVELOPMENT WITHOUT COMPROMISING RESIN COMPOSITE'S FINAL PROPERTIES.

ABSTRACT

Objectives: Stress development during the polymerization process continues to be a major factor that limits predictability and longevity of resin composite restorations. This study evaluated the effect of the photoinitiator type on the maximum rate of polymerization (R_p^{max}), stress development (final stress and maximum rate, R_{stress}^{max}), degree of conversion (DC) and cross-link density (CLD) of materials containing camphorquinone (CQ), phenylpropanedione (PPD) or CQ/PPD. **Materials and methods:** R_p^{max} was evaluated via differential scanning calorimetry (DSC). Contraction force measurement was assessed with a single cantilever device for five minutes. The samples were subsequently tested by infrared-spectroscopy to evaluate the DC. After, samples were soaked in ethanol to evaluate the swelling coefficient (α) as a way to estimate the CLD. The results were analyzed by one-way ANOVA and Tukey's test ($p = 0.05$). **Results:** CQ showed the highest R_p^{max} and R_{stress}^{max}. PPD produced the lowest DC and the highest α. The mixture CQ/PPD produced statistically lower R_p^{max} and R_{stress}^{max} than CQ alone, but similar DC and CLD. **Conclusion:** CQ/PPD reduced the R_p^{max} and R_{stress}^{max} without a reduction in DC and CLD. Therefore, the use of alternative photoinitiator systems could be a promising way to reduce the stress developed during the composite's polymerization without affecting the final properties.

INTRODUCTION

The stress development resulting from the polymerization process is the major drawback of dental composite restorations. Thus, special attention has been taken in order to develop techniques and materials that are able to reduce it [1].

The stress arises from multiple factors [2]. Basically, a volumetric shrinkage occurs simultaneously with elastic modulus development, as the length and the cross-link density of the polymer chains increase [3, 4]. In this way, the polymerization reaction, the material's formulation and the boundary conditions (bonding conditions, cavity configuration, and substrate compliance) all play essential roles in stress development and/or transmission to tooth structures [5-11].

In order to diminish the stress development in photoactivated composites, specific light exposure methods have been proposed as a way to reduce the rate of polymerization [12, 13]. In theory, stress release by viscous flow before the vitrification stage would be allowed to occur without compromising the final polymer properties [14, 15]. However, there are contradictions about the proposed advantages: i) the material's ability to flow (deformation) is questionable because the majority of the shrinkage stress is developed during and after the vitrification stage and, therefore, opportunity for polymer relaxation would be restricted for clinical time scales for light activation [11]; ii) the final degree of carbon double-bond conversion (DC) tends to be lower when real-time readings are performed during the stress evaluation [16], and iii) the lower rate of polymerization decreases the cross-link density (CLD), resulting in greater softening in solvents [17, 18] and/or lower final elastic modulus [19]. However, cross-linked dimethacrylate polymers have been characterized under controlled conditions and the polymer structure was not affected by the rate of polymerization [20].

Besides managing light exposure, changes in the resin composite formulation have also been tested to reduce contraction stress [1]. However, very little has been done regarding the photoinitiator system. Similar to the photoactivation protocols, the concentrations of camphorquinone (CQ, the most common photoinitiator) and inhibitors may be varied to reduce the rate of polymerization whithout affecting other properties [21]. Braga and Ferracane [22] tested experimental materials with different concentrations of inhibitor, and showed that increased inhibitor concentrations reduced the rate of polymerization and the shrinkage stress without significantly compromising the final DC. However, it must be noted that that in this study, the DC tended to be lower for mixtures containing higher amounts of BHT than those with lower content of the inhibitor and the specimens used for the spectroscopy measurements were cured under different conditions than those cured in the stress measuring device.

Recently, it was demonstrated that the addition of the photoinitiator phenylpropanedione (PPD), increased the polymerization efficiency and reduced the yellowing effect provided by CQ [23, 24], while producing lower shrinkage and polymerization rates than CQ [25, 26]. However, there is no evidence that the stress development is also reduced. Therefore, the objectives of the present investigation were: 1) to investigate the reaction kinetics of composites containing CQ, PPD and the mixture CQ/PPD, 2) to measure the polymerization stress development by these materials, and 3) to evaluate the resulting DC and the CLD. The CLD was assessed by measuring the swelling coefficient, α, in ethanol [18]. The hypothesis tested was that PPD alone or the mixture CQ/PPD produces lower maximum rate of polymerization (R_p^{max}) and maximum rate of stress (R_{stress}^{max}) development than CQ alone, without reduction in the final DC and CLD.

MATERIALS AND METHODS

Composite preparation

Monomer mixtures of 2,2 bis[4-2(2-hydroxy-3-methacroyloxypropoxy)phenyl] propane (Bis-GMA, Esstech, Essington, PA, USA) and triethyleneglycol dimethacrylate (TEGDMA, Esstech) were prepared in the ratio of 50/50 by weight percentage (wt%). Two photoinitiators were used to make the resin photo-curable: CQ (Polysciences Inc., Warrington, PA, USA) and 1-phenyl-1,2- propanedione, PPD (Aldrich Chem. Co., Milwaukee, WI, USA). Ethyl 4-dimethylaminobenzoate (EDMAB, Avocado, Heysham, Lanchire, UK) was used as co-initiator and 2,6-Di-*tert*-butyl-4-methyl-phenol (BHT, Aldrich) was used as inhibitor at a constant amount (0.05 wt%). The percentage (in mol) of photoinitiator and co-initiator tested are shown in Table 1. The photoinitiator/co-initiator relationship at 1:2 was chosen after a pilot study. This relationship demonstrated the best properties (DC, hardness and solubility) when compared with 2:1, 1;1, 1:1.5, regardless of the photoinitiator type (CQ, PPD and the mixture CQ/PPD).

Resins were loaded with strontium glass fillers (4.0 µm average size; 3% silane level) (provided by Bisco Inc., Schaumburg, IL, USA)) at a total content of 80 wt%. All the components were homogeneously mixed for one minute at 1300 rpm (DAC 150 Speed Mixer, Flacktek, Landrum, SC, USA). All materials were prepared and handled under a yellow safe light, and used within one week after mixing.

Reaction kinetics characterization

A differential scanning calorimeter (DSC 7, Perkin-Elmer Inc., Wellesley, USA) was used to follow the polymerization reaction kinetics at a temperature of 25 ± 0.01°C (n=3). Ten milligrams (±0.1 mg) of resin composite was spread as a thin layer (≈ 130 μm) and polymerized in standard aluminum pans with the three light exposures. The reaction kinetics were evaluated by recording the three thermograms under nitrogen atmosphere (20 psi) and constant water flow. The first peak represented the exothermic change generated by the composite polymerization plus the heat released from the light curing unit (LCU). The two following peaks represented only the heat released from the LCU. The heat of polymerization was determined by subtracting the average heat value of the two last peaks from the first peak value. Each exposure consisted of 40 seconds of light at 315 mW/cm^2. This value was measured through the DSC cap, which was positioned between the LCU (VIP, Bisco Inc., Schaumburg, IL, USA) and a power meter sensor (Powermax 5200, Molectron, Portland, OR, USA).

The DC at different times was determined from changes in heat release during the experiment. By registering the heat values and changes over time, conversion changes were calculated from the theoretical heat release per mole reacted from the carbon double bond (56 kJ/mol) over the time course of the experiment. Therefore, the derivative DC/ time was calculated as the rate of polymerization, the highest value in the spreadsheet was the R_p^{max} and the moment when it occurred was the peak time of R_p^{max}. The parameters DC, R_p^{max}, DC at R_p^{max} and the peak time of R_p^{max} were used to compare the formulations.

Stress development evaluation

The Bioman stress measurement device has been described previously in detail [9]. The system is based on a cantilever load-cell (500 kg) fitted with a rigid integral clamp (Figure 1). The compliant end of the cantilever held a circular steel rod (10 mm diameter X 22 mm long) vertically and perpendicular to the load-cell axis. The counter-face consisted of a removable rigid glass plate that was held rigidly relative to the base-plate in a special clamp during measurement. The lower end of the steel rod was sand-blasted, and in contrast to the original methodology described by Watts *et al.* [9], the surface of the glass-plate opposing the steel-rod was only silanated (3M/ESPE Dental Products, St Paul, MN 55144, USA)) (instead of sandblasting + silanation). The composite was then introduced between the plate and vertical rod to form an uncured specimen-disk of 10 mm diameter and 0.8 mm thickness (which represents a bonded to non-bonded surface area, i.e. C-factor, of 6.25). The composite specimen was irradiated through its thickness dimension from below by the LCU (VIP) for 40 s at 800 mW/cm^2, as measured with the power meter.

The load-signal from the cantilever cell was amplified and the signal was acquired by a standard computer. The registered load (in Newton, N) was then divided by the disk area (10 mm) in order to obtain the stress values (MPa). Subsequently, as in previous studies [9, 27], the raw stress data were treated by a “correction factor” of 4 in order to relate the present data to a lower compliance system, such as a human tooth cusp. Measurements were performed during 5 minutes after the photoactivation procedure. Each group contained six samples (n=6). Maximum stress, maximum rate of stress development (R_{stress}^{max}) and time when R_{stress}^{max} occurred (peak time) were determined.

Degree of carbon double–bond conversion measurements

Immediately after the stress development evaluation, the cured specimen was carefully removed from the *Bioman* and infrared spectroscopy (FTIR) was used to determine its DC. Were required 5 minutes to remove the sample from the *Bioman*, so the DC was evaluated around 10 minutes after the start of the photoactivation procedure.

Small chips of composite were removed with a scalpel from the surface of the sample and were placed on a KCl crystal for transmission spectroscopy (DS20/XAD microscope, Analect Instruments, Irvine, CA, USA). Thirty scans were taken at 8 cm^{-1} resolution. Five measurements were made with chips removed from different regions of the surface and an average DC value was calculated. This procedure was done for the two surfaces, the one that was in contact with the glass plate and the one in contact with the steel rod. The average of these two surfaces was considered for each sample to provide a more accurate representation of the cure through the specimen.

The paste of the uncured composite was similarly tested. DC was calculated from the ratio of the C=C peak from the methacrylate group to that of the unchanging C…C peak from the aromatic ring for the uncured and cured specimens using the standard baseline technique.

Swelling coefficient determination

This methodology was modified from the original version described by Neumann *et al.* [17]. After DC analysis, the samples were immersed in absolute ethanol at room temperature until an equilibrium weight was reached. Then samples were removed and the excess solution was quickly dried with blotting paper, before the samples were re-weighed. The swelling coefficient (α) values were calculated by the following formula:

$\alpha = [M_{eq} - M_0 / M_0]\ [1/d_s]$

where M_{eq} is the mass of the saturated sample (polymer + solvent) after equilibrium, M_0 is the mass of the polymer before immersion and d_s is the density of the solvent (absolute ethanol = 0.789 g/mL).

Statistical Analyses

The results were analyzed by one-way analysis of variance (ANOVA) and Tukey's tests ($p = 0.05$).

Pearson's correlation tests and regression analyses were done to establish the relationships between: a) maximum rate of polymerization (R_p^{max}) and maximum rate of stress (R_{stress}^{max}), b) peak time of R_p^{max} and peak time of R_{stress}^{max}, c) R_p^{max} and maximum stress, d) DC (from samples removed from the Bioman) and maximum stress, e) R_{stress}^{max} and maximum stress, f) DC and α, and g) R_p^{max} and α. The mean values of each group used for comparison.

RESULTS

Reaction kinetics characterization

Mean values of DC, R_p^{max}, DC at R_p^{max} and the peak-time reaction are shown in Table 2. The composite formulated with only PPD showed lower DC than the others. There was a significant difference among the R_p^{max} data produced by all groups, where CQ > CQ/PPD > PPD. There was no difference in DC at R_p^{max} among the groups; but the reaction peak-time for CQ occurred before those from CQ/PPD and PPD.

Polymerization contraction stress development

The maximum stress, R_{stress}^{max} and peak-time at R_{stress}^{max} mean values are given in Table 3. There were no significant differences among the maximum stress values obtained from the different resin composites. However, the resin composite formulated with CQ produced the highest R_{stress}^{max} as well as the lowest reaction peak-time.

Degree of carbon double–bond conversion and swelling coefficients from the samples removed from the stress measurement device

Table 4 shows the mean values of DC obtained from the FTIR analysis and swelling coefficient after ethanol soaking. The composite formulated with PPD alone produced the lowest DC, while those formulated with CQ alone and the combination CQ/PPD produced statistically similar DC ($p<0.05$).

The swelling test showed that the composite formulated with CQ produced lower swelling than that with PPD, while that with CQ/PPD produced intermediate values.

Correlations

The correlation tests showed high positive correlations between (a) R_p^{max} and R_{stress}^{max} ($r = 0.966$) and (b) peak time of R_p^{max} and peak time of R_{stress}^{max} ($r = 0.929$). A weak inverse correlation was found for (c) the DC and maximum stress ($r = -0.573$), while (d) the R_p^{max} and the maximum stress ($r = -0.934$) as well as (e) R_{stress}^{max} and maximum stress ($r = -0.811$) demonstrated a strong inverse relationship. DC and swelling coefficient ($r = -0.970$) (f), as well as (g) R_p^{max} and swelling coefficient ($r = -0.9704$), demonstrated a strong inverse relationship.

DICUSSION

The hypothesis tested, that alternative photoinitiator systems produce lower R_p^{max} and R_{stress}^{max} than CQ alone, without reduction in the final DC and CLD, was accepted. PPD alone and the mixture CQ/PPD reduced the R_p^{max} and R_{stress}^{max}, but only the mixture CQ/PPD resulted in similar DC and CLD than CQ alone.

Reaction kinetics

The DSC results demonstrated that PPD alone produced the lowest R_p^{max} but also compromised the final DC (Table 2), while the mixture CQ/PPD reduced the R_p^{max} by 10 % without compromising the final DC. These findings are probably related not only to the light absorption characteristics by the photoinitiator but also its' characteristic photochemistry.

A pilot study showed that PPD alone absorbed less energy emitted from the VIP LCU than CQ alone. Therefore, the presumption of Emami and Söderholm [26], that the reduced overlap between the PPD absorption spectra and the LCU emission spectra partially explains the lower reactivity of PPD formulations, is probably correct. However, the results obtained with the mixture CQ/PPD shows that the photochemistry characteristics of the molecules also play essential role.

Park et al. [23] suggested two reasons for a synergistic effect between the molecules CQ and PPD. First, CQ operates by hydrogen abstraction from the amine molecule, while PPD undergoes photo-cleavage and proton abstraction, and thus the two methods are not necessarily competing. Second, the combination of the two types of molecules present wider absorption spectra for the curing light. However, in the present investigation, the mixture CQ/PPD was tested at the same total concentration as each photoinitiator alone and produced lower R_p^{max} than CQ alone, thereby showing decreased reactivity. Since the pilot data demonstrated that the mixture CQ/PPD exhibited similar absorption from the VIP LCU as CQ alone, the lower reactivity might be attributed to other factors. Indeed, it was recently demonstrated that PPD produced a lower rate of polymerization than CQ even in a situation where the spectra of the LCU was better correlated with the PPD [28]. The authors attributed this effect to a lower quantum yield of PPD, despite another study [24] that showed a higher quantum yield for PPD when compared with CQ. Another hypothesis could be that the PPD molecule has lower affinity for the amine molecule, which might reduce overall free-radical generation, but further investigation is needed to clarify the effect.

The photoinitiator type did not influence the DC at the R_p^{max}. Basically, the R_p^{max} occurred around 13 % of conversion for all the tested groups. This phenomenon, known as the "gel effect", is characteristic of composites that become viscous very fast, making the rest of the polymerization reaction proceed by chain diffusion [11]. On the other hand, the peak time of reaction was delayed when the composites were formulated with PPD or CQ/PPD (≈ 1 second later than CQ). This behavior is characteristic of a slower reaction as a consequence of fewer free-radical centers and/ or lower reactivity of the species [29].

Stress development

The results showed that the speed of stress development could be significantly reduced if the alternative photoinitiator systems were used. Basically, the use of PPD alone and/or CQ/PPD reduced the R_{stress}^{max} by about 51% and 29%, respectively compared to CQ alone, whereas the peak time of R_{stress}^{max} was delayed by about 56% and

44%, respectively. These outcomes are strongly correlated with the reaction kinetics, where a positive relationship was observed between the R_p^{max} and R_{stress}^{max}, as well as between the peak times at R_p^{max} and at R_{stress}^{max} ($r = 0.966$ and $r = 0.929$, respectively). This agrees with previous statements that the rate of stress development might be dictated by the polymerization reaction kinetics [30]. Consequently, factors affecting free radical generation by the different photoinitiators will also affect reaction kinetics, and thus help to explain the slower stress development.

The correction factor was applied to the stress values to make the data fit a more conservative estimation of cuspal displacement and to compare the results of the current investigation with those obtained in a previously published study with the *Bioman* device [9]. The maximum stress values ranged between 3.55 and 7.86 MPa, which closely approximate the results obtained by Watts et al. [9], which ranged between 4.82 and 7.30 MPa (for Clearfil AP-X and Point-4, respectively) when using 0.8 mm thick specimens.

Though the maximum stress values registered during the five minute testing period were not statistically different, the values tended to be higher for systems with lower DC, R_p^{max} and/ or R_{stress}^{max}. These inverse correlations (DC and maximum stress, $r = -0.573$; R_p^{max} and maximum stress, $r = -0.934$; R_{stress}^{max} and maximum stress, $r = -0.811$) contradict previous findings that stress development is dependent on these factors when tested in low compliance systems [16, 22]. Since the values registered by the load cell are influenced by the elongation of the testing device (the system allows deformation ≈ 6 μm/MPa [9]), it is possible that the materials with higher R_p^{max} and R_{stress}^{max} also generated higher deformation of the system components until the maximum rate point was reached, thus relieving most of the stress. Although detachment of the sample from the specimen holder could be expected for these systems if high enough loads are produced, the maximum values achieved may have remained within the threshold range for secure bonding.

Degree of carbon double – bond conversion and swelling coefficients

The FTIR readings and the swelling coefficient determinations of the samples removed from the *Bioman* were performed because it has been postulated that the methods used to reduce the stress development might affect the final DC [16] and/or the cross-linking density [17, 19]. While the PPD alone produced a polymer with lower DC and higher swelling coefficient than CQ alone, the combination CQ/PPD did not compromise the final DC and/or the swelling coefficient, but it did decrease the R_p^{max} and R_{stress}^{max}.

The present outcomes are in agreement with the statement that polymer cross-link density is more dependent on the final DC than on the rate of polymerization [20], as CQ and CQ-PPD showed similar DC but different R_p^{max}. On the other hand, despite the similar swelling coefficients produced by the CQ alone and the combination CQ/PPD, the data suggest a tendency for the swelling coefficient to increase with lower R_p^{max} (R_p^{max} and swelling coefficient, r = -0.939). This would lend support to the statement that polymers with similar DC could exhibit different cross-linking density patterns due to differences in the rate of polymerization [17, 19].

Indeed, the CQ/PPD combination diminish the rate of stress development, as well as delaying its peak time, and without compromising the final DC and swelling coefficient when compared with CQ alone. Thus the mixture of both photoinitiators could be an interesting way to reduce the speed of reaction, and consequent stress, without compromising the final polymer structure.

CONCLUSIONS

The hypothesis was accepted. Under the conditions used in the present investigation, composites formulated with the mixture CQ/PPD produced lower R_p^{max} and R_{stress}^{max} than that with CQ alone without compromising the final DC and CLD.

ACKNOWLEDGMENTS

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Table 1: Photoinitiator/co-initiator systems tested in the present investigation (concentration in mol%).

Group	**Photoinitiator type (concentration in mol %)**	**Co-initiator (concentration in mol %)**
1 (control)	CQ (0.6)	EDMAB (1.2 mol %)
2	CQ/PPD (0.3/ 0.3)	EDMAB (1.2 mol %)
3	PPD (0.6)	EDMAB (1.2 mol %)

Table 2: Mean values of degree of conversion (DC), maximum rate of polymerization (R_p^{max}), DC at R_p^{max} and peak time at R_p^{max}.

Photoinitiator	**DC (%)**	**R_p^{max} (%/sec)**	**DC at R_p^{max} (%)**	**Peak time of R_p^{max} (sec)**
CQ	62.11 (0.46) ^{a}	3.3 (0.1) ^{a}	12.24 (1.26) ^{a}	6
CQ/PPD	64.01 (2.34) ^{a}	3.0 (0.0) ^{b}	12.79 (1.24) ^{a}	7
PPD	59.58 (1.04) ^{b}	2.4 (0.1) ^{c}	14.37 (0.12) ^{a}	7

Numbers in parenthesis are standard deviations. Mean values followed by different letters in a column are significantly different ($p<0.05$).

Table 3: Stress development measured in the Bioman. Mean values of maximum stress, maximum rate of stress (R_{stress}^{max}) and peak-time at R_{stress}^{max}.

Photoinitiator	**Maximum stress (MPa)**	**R_{stress}^{max} (MPa/sec)**	**Peak-time at R_{stress}^{max} (sec)**
CQ	4.69 (1.14) ^{a}	5.75 (1.18) ^{a}	2.21 (0.65) ^{b}
CQ/PPD	5.96 (1.14) ^{a}	4.09 (0.36) ^{b}	3.98 (0.45) ^{a}
PPD	6.10 (1.76) ^{a}	2.79 (0.80) ^{b}	5.03 (0.96) ^{a}

Numbers in parenthesis are standard deviations. Mean values followed by different letters in a column are significantly different ($p<0.05$).

Table 4: Mean values of DC obtained from the FTIR and swelling coefficients. Evaluation performed at the samples removed from the stress measurement device.

Photoinitiator	**Degree of conversion (%)**	**Swelling coefficient (mL/g)**
CQ	52.79 (1.64) ^{a}	0.004 (0.001) ^{a}
CQ/PPD	52.81 (1.69) ^{a}	0.005 (0.002) ^{ab}
PPD	46.92 (2.24) ^{b}	0.008 (0.002) ^{b}

Numbers in parenthesis are standard deviations. Mean values followed by different letters in a column are significantly different ($p<0.05$).

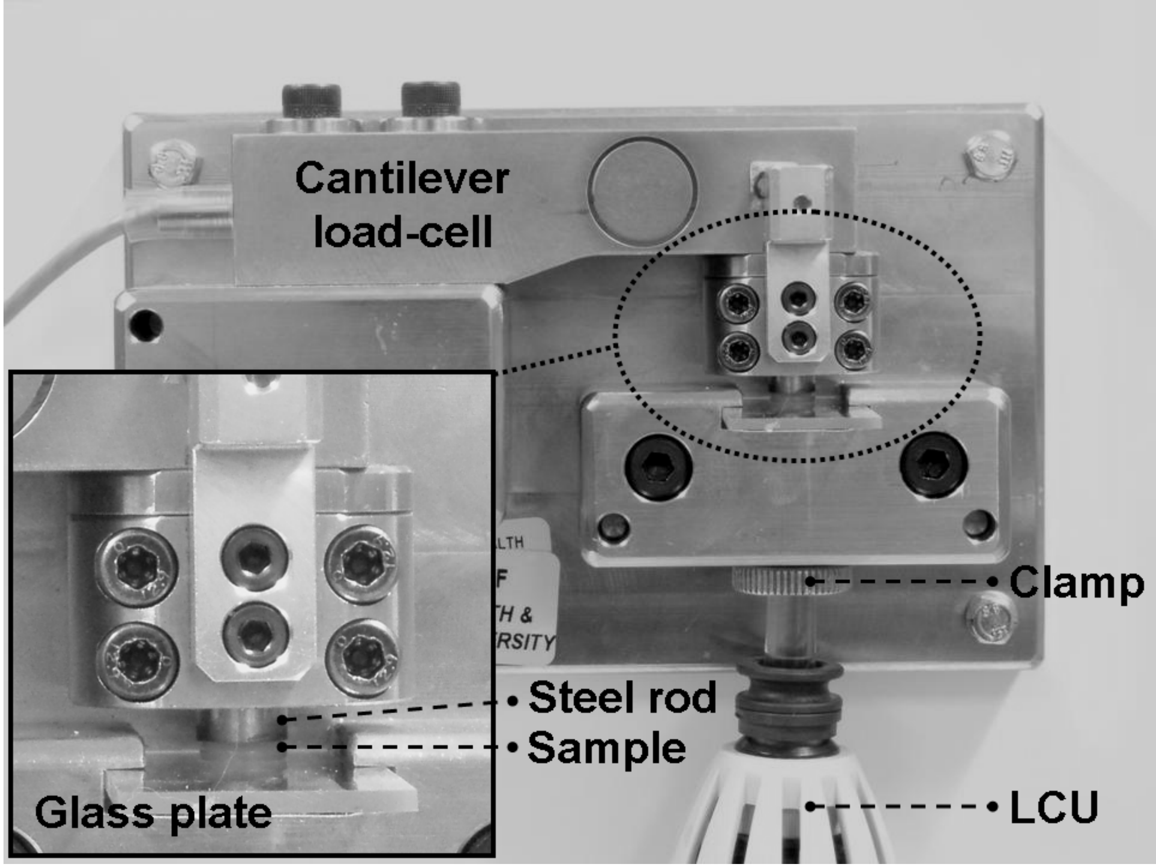

Figure 1: The *Bioman* stress measurement device.

CONSIDERAÇÕES GERAIS

O uso de sistemas fotoiniciadores alternativos pode parecer um contra-senso à evolução das fontes de luz emitida por diodos (LEDs), os quais trazem como grande vantagem o espectro de emissão centrado na absorção da CQ. No entanto, o desenvolvimento de LEDs com emissão de luz num espectro mais amplo (ou de dois picos de emissão) mostra o quanto os fabricantes visam a necessidade de fontes de luz capazes de sensibilizar estas moléculas. Além disso, recentes estudos realizados por pesquisadores de empresas de materiais odontológicos (VOGEL & RHEINBERGER, 2007; MOSZNER *et al.*, 2007) sinalizam o quanto sistemas fotoiniciadores alternativos dispõem de aplicabilidade no mercado atual.

Considerando o estudo descrito no Capítulo 1, fica clara a importância da densidade de potência absorvida (PD_{abs}) na cinética de reação e propriedades finais do polímero formado quando considerada a comparação entre CQ e PPD (dentro de limites impostos pela própria cinética de polimerização). Por outro lado, apesar dos sistemas CQ e CQ/PPD apresentarem semelhantes valores de PD_{abs}, diferentes valores de taxa de polimerização foram encontrados. Assim, esta diferença de reatividade pode ser resultante dos diferentes mecanismos de formação dos radicais livres a partir das moléculas de CQ e PPD. Esta afirmação é suportada pelos recentes achados de SCHROEDER, COOK & VALLO (2007), os quais mostraram que mesmo em situações onde a PD_{abs} era 40% maior para o sistema PPD, a CQ ainda apresentava maior taxa de polimerização.

A relação entre fotoiniciador e co-iniciador de 2:1 em peso, utilizada no primeiro estudo, foi baseada na experiência adquirida com estudos prévios realizados com o sistema CQ/ EDMAB (PARK, FERRACANE & MUSANJE, 2004; CHEN, FERRACANE & PRAHL, 2006). Entretanto, após análise dos resultados obtidos, verificou-se a necessidade de testes adicionais a respeito da relação fotoiniciador/ co-iniciador, tanto para a CQ, quanto para a PPD; sendo este o objetivo do estudo descrito no Capítulo 2.

O efeito da concentração de amina empregada nas propriedades de compósitos formulados com CQ, PPD ou CQ/PPD é descrito no Capítulo 2. Enquanto os primeiros estudos realizados com o PPD sugerem que a taxa de amina não seria fundamental para este fotoiniciador (PARK, CHAE & RAWLS, 1999; SUN & CHAE, 2000; NEWMANN *et al.*, 2006), os presentes resultados mostram o contrário, concordando com os recentes achados de EMAMI & SÖDERHOLM (2005) e SCHROEDER, COOK & VALLO (2007). Desta forma, as diferenças aqui mencionadas provavelmente estão relacionadas ao tipo de molécula utilizada como co-iniciador e/ ou às condições experimentais empregadas.

Após análise dos resultados obtidos nos estudos dos Capítulos 1 e 2, ficou evidente que a grande vantagem na utilização da PPD seria uma hipotética redução na geração de tensões inerentes do processo de polimerização. Assim, o estudo descrito no Capítulo 3 teve como objetivo avaliar a tensão gerada, e as conseqüentes propriedades do polímero formado, quando diferentes sistemas fotoiniciadores são utilizados.

Diferentemente dos estudos descritos nos Capítulos 1 e 2, as formulações testadas no estudo descrito no Capítulo 3 foram compostas de uma porcentagem de carga em níveis de 80 % em peso para que houvesse uma menor capacidade de escoamento do material, o que poderia resultar numa redução dos valores finais de tensão, mascarando os resultados. Desta forma, diferenças de valores encontradas nos capítulos anteriores para os dados do DSC podem ser resultantes de diferenças no conteúdo inorgânico (nos estudos descritos nos Capítulos 1 e 2 foram utilizados materiais contendo 60% em peso), pois a alteração do conteúdo de carga também alteraras propriedades térmicas do material, como a condutividade e a difusividade térmica.

Basicamente, se comparado à CQ isolada, o sistema fotoiniciador CQ/PPD reduziu a taxa máxima de desenvolvimento da tensão de polimerização, bem como o momento em que esta ocorre. Assim, mudanças na composição do sistema fotoiniciador poderiam ser utilizadas como forma de reduzir o desenvolvimento da tensão gerada na zona de união compósito/ adesivo/ dente. Além disso, o uso da CQ combinada à PPD produziu valores de grau de conversão e de densidade de ligações cruzadas similares aos produzidos apenas com a CQ.

Um fato que deve ser levado em consideração é a influência da capacidade de deformação do sistema de leitura ("compliance") (FEILZER, DE GEE & DAVIDSON, 1987; MIGUEL & DE LA MACORRA, 2001; LAUGHLIN *et al.*, 2002; WATTS, MAROUF & AL-HINDI, 2003; BRAGA, BALLESTER & FERRACANE, 2005; FERRACANE, 2005; LEE *et al.*, 2007; WITZEL *et al.*, 2007). Apesar do aparato utilizado (*Bioman*) ser considerado um sistema que permite deformação, diferenças significantes foram registradas. Assim, pode-se especular que uma maior diferença poderia ocorrer em situações de menor capacidade de deformação.

Finalizando, os resultados do presente estudo demonstram a complexidade que envolve a aplicação dos sistemas fotoiniciadores alternativos nas formulações de compósitos odontológicos. Fatores como cinética de reação, fotoquímica e óptica exercem grande influência sobre os resultados. Além disso, foi possível verificar que pequenas modificações no sistema fotoiniciador são responsáveis por grandes alterações no polímero resultante.

CONCLUSÕES GERAIS

De acordo com os materiais e métodos empregados no presente estudo, foi possível concluir que:

1. O uso da PPD e da combinação CQ/PPD foi capaz de promover semelhante grau de conversão do que CQ. Entretanto, com valores inferiores de taxa de polimerização. O uso da PPD reduziu os valores de dureza. Menor valor no grau de amarelo foi possível apenas quando a PPD foi utilizada em baixa concentração. Além disso, ficou evidente que os valores de grau de conversão, taxa de polimerização e dureza foram dependentes da densidade de potência absorvida. No entanto, fatores como a cinética de reação e interação do fotoiniciador com o co-iniciador também exercem forte influência.
2. O desempenho da PPD, assim como da CQ, foi dependente da taxa de amina empregada na formulação. A taxa de amina não teve influência no grau de amarelo para formulações contendo PPD. Por outro lado, para as formulações contendo CQ, o grau de amarelo foi maior nos períodos iniciais e estabilizou após estocagem em água.
3. O uso da PPD associada à CQ produziu menores valores de taxa máxima de desenvolvimento de tensão do que apenas CQ sem reduzir o grau de conversão e a densidade de ligações cruzadas.

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ANEXO 1

CARTA DE ENVIO DO CAPÍTULO 1 PARA PUBLICAÇÃO

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Action Links	DEMA-D-07-00477	Photoinitiator type affects rate of polymerization, degree of conversion, hardness and yellowing of dental resin composites.	Dec 10, 2007	Dec 10, 2007	Under Review

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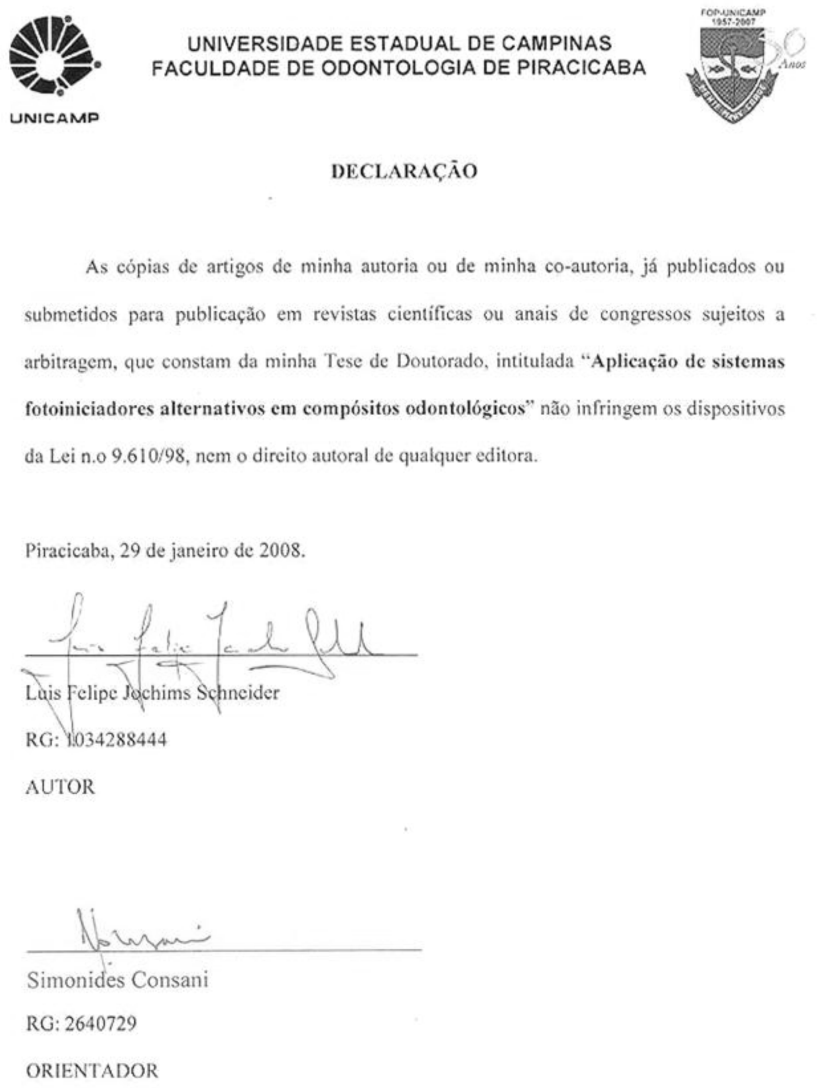
ANEXO 2

DECLARAÇÃO DE DIREITOS AUTORAIS



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