

Polymerization capability of simplified dental adhesives with camphorquinone, phenyl-propanedione and bis-alkyl phosphine photoinitiators

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Aim: this study aimed to evaluate the degree of conversion (DC) exhibited by novel formulations of dental adhesive systems including camphorquinone (CQ), phenyl-propanedione (PPD), and bis-alkyl phosphine oxide (BAPO) when cured by mono- or polywave light emitting diodes (LEDs). **Methods:** an adhesive model was formulated by mixing hydroxyethyl methacrylate (HEMA, 40 wt%) and bisphenol A glycidyl dimethacrylate (BisGMA, 60 wt%) in ethanol (30 wt%). Five materials were then formulated by adding the following photoinitiators: CQ (1 mol%), CQ/PPD (0.5/0.5 mol%), CQ/BAPO (0.5/0.5 mol%), PPD (1 mol%), and BAPO (1 mol%). The DC for each material was measured with Fourier transform infrared spectroscopy. Analysis of variance and Tukey's post-hoc test were used to analyze the data ($p < 0.05$). **Results:** Except for CQ, the photoinitiators provided a significantly higher DC in the adhesive systems following photoactivation with a polywave LED. **Conclusion:** The use of alternative photoinitiators and a polywave LED improved the DC of the adhesive systems examined.

Keywords: Spectroscopy, fourier transform infrared. Dental materials. Dental cements.

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Received: March 06, 2018

Accepted: July 09, 2018



Introduction

Dental adhesives are materials composed of monomers with both hydrophilic and hydrophobic groups, photoinitiators, inhibitors or stabilizers, solvent and, in some cases, inorganic fillers¹. The classical model of dental adhesives is available in three application steps (acid etching, priming and bonding). Over time, the need to reduce the number of clinical steps during application of dental adhesives required the emergence of simplified materials to reduce the chair time. In this way, adhesives systems have gone through several changes in recent years, with the creation of new monomers and photoinitiating molecules, in an attempt to simplify bonding procedures without compromising adhesion to tooth substrates².

In general, the adhesive performance depends on the degree of conversion (DC), so that a high DC is fundamental to improving resistance of material degradation under *in vivo* clinical conditions. Low DC of dental adhesives is associated with high water sorption/solubility, as well as low bond strength values, low mechanical properties, increased permeability, and even the occurrence of phase separation³. This conversion could be affected by many factors, including the photoinitiator systems and light wavelength of the curing unit used⁴. Thus, the development of simplified adhesive systems capable to show increased DC is detrimental.

The most contemporary adhesive systems are activated by light within the blue band of the spectrum (400–500 nm) and they use camphorquinone (CQ) as a photoinitiator⁵. CQ is a solid yellow compound with an unbleachable chromophore group that can absorb light in the spectral range of approximately 400–500 nm, with a peak near 470 nm^{6,7}. However, the yellow hue characteristic of CQ compromises its aesthetic performance and photoinitiators eventually degrade over time^{5,8}. Therefore, alternative photoinitiators such as phenyl propanodione (PPD), and bis-alkyl phosphine oxide (BAPO) have been investigated in an attempt to replace CQ or decrease the amount of CQ into dental materials without compromising the DC^{6,9,10}.

Most of the alternative photoinitiators that have been studied have an absorption peak in the ultraviolet region which extends slightly into the visible light spectrum (380–420 nm)^{5,11}. Both the spectrum emitted by a light source and the absorption capacity of a photoinitiator have an effect on the polymerization process of composites, thereby influencing their properties^{5,11,12}. As a result, cure efficiency can be compromised when narrowband light-emitting diodes (LEDs), such as conventional monowave LEDs are used, since these LEDs do not have light emission in the violet wavelength range^{5,11,13}. Thus, the ability of conventional LEDs to activate photoinitiators that respond to ultraviolet light is limited. However, polywave LEDs emit dual peaks, with one additional peak being near 405 nm^{14–16}, and this allows these LEDs to activate photoinitiators such as PPD and BAPO.

In this way, the aim of this study was to evaluate the degree of conversion (DC) of novel formulations of dental adhesive systems including CQ, PPD, and BAPO when cured by mono- or polywave LEDs in order to test the hypothesis that the use of alternative photoinitiators and photoactivation with a polywave LED can lead to an increased DC.

Materials and methods

Experimental design

The response variable evaluated in this *in vitro* study was DC. Five photoinitiators (CQ, CQ/PPD, CQ/BAPO, PPD, and BAPO) (Table 1) and two types of LEDs (monowave and polywave) (Table 2) were tested.

Table 1. Characteristics of photoinitiators used in this study.

| Photoinitiator | Absorption spectrum range (nm) | Absorption intensity peak (nm) ^[7] | Molar extinction coefficient (L/mol cm) ^[7] |
|----------------|--------------------------------|---|--|
| CQ* | 400 – 500 ^[7] | 470 | 28±2 |
| PPD** | 350 – 480 ^[17] | 398 | 150±10 |
| BAPO*** | 365 – 416 ^[7] | 370 | 300±10 |

*Camphorquinone; **Phenyl-Propanedione; ***Bis-Alkyl Phosphine Oxide

Table 2. Technical details of light emitting diodes used in this study according to the manufacturers.

| Comercial name/ Manufacturer | Classification | Spectrum range | Intensity peaks | Irradiance |
|---|----------------|---|------------------|-------------------------|
| Bluephase G2, Ivoclar Vivadent, Schaan, Liechtenstein | Polywave | 385 - 515 nm (380 - 420; 420 - 490) | 405 nm 460 nm | 1200mW/cm ² |
| Radii Cal, SDI, Victoria, Australia. | Monowave | 440 - 480 nm | 460 nm | 1313 mW/cm ² |

Formulation of the experimental adhesive systems

Bisphenol A glycidyl dimethacrylate (BisGMA) and hydroxyethyl methacrylate (HEMA) (60:40 wt%) (Sigma-Aldrich, St. Louis, MO, USA) were mixed with ethanol (30 wt%)¹⁷. Then, five different materials were generated with the addition of these various photoinitiators: CQ (1 mol%), CQ/PPD (0.5/0.5 mol%), CQ/BAPO (0.5/0.5 mol%), PPD (1 mol%), and BAPO (1 mol%). Ethyl 4-(dimethylamino)benzoate (EDMAB) (Sigma-Aldrich) (1 mol%) was added to all of the prepared formulations to serve as a co-initiator.

DC evaluation

DC was evaluated with a Fourier transform infrared/attenuated total reflectance instrument (FTIR/ATR) (Spectrum 100, PerkinElmer, Shelton, CT, USA) at 24 °C under 64% relative humidity. One drop of each adhesive system (n = 10 per photoinitiator and LED) was applied to the ATR surface and the solvent was evaporated for 10 s. Then, a thin glass plate (0.5 mm thick) was placed on the material and it was photo-activated for 10 s using a LED. The irradiance of the LEDs were measured by using a computer-controlled spectrometer (USB2000, Ocean Optics, Dunedin, USA) and was integrated using Origin 6.0 software (OriginLab, Northampton, USA).

The absorption spectra of both the nonpolymerized and polymerized adhesive systems prepared were obtained between 4000 and 650 cm⁻¹ with 32 scans at 4 cm⁻¹. Intensities of the aliphatic carbon-to-carbon double-bond absorbance peak (located

at 1638 cm⁻¹) and the aromatic component (located at 1608 cm⁻¹; reference peak) were recorded. DC (%) was calculated using the following equation¹⁸:

$$DC (\%) = 100 \times [1 - (\frac{R_{\text{polymerized}}}{R_{\text{nonpolymerized}}})],$$

where R represents the ratio between the absorbance peaks at 1638 cm⁻¹ and 1608 cm⁻¹.

Statistical analysis

Two-way analysis of variance (ANOVA) and Tukey's post-hoc test were used ($p < 0.05$).

Results and Discussion

There were statistically significant differences in the interaction between photoinitiators x LEDs ($p < 0.01$). Table 3 shows the intergroup comparisons. Only the CQ adhesive system achieved a similar mean DC as the samples were photoactivated by Radium Cal and Bluephase G2, so that Bluephase G2 provided a higher mean DC than Radium Cal to the other adhesive systems. Bluephase G2 provided similar mean DC between adhesive systems. Radium Cal provided the highest DC to the CQ adhesive system, while the lowest DC was observed for the CQ/BAPO and BAPO adhesive systems. Thus, the hypothesis that the use of alternative photoinitiators that and photoactivation with a polywave LED can lead to an increased DC was accepted.

Table 3. Degree of conversion (%) means (standard-deviation) of dental adhesive systems according to the photoinitiator system and the curing light.

| Photoinitiator system | Light emitting diode | |
|-----------------------|----------------------|----------------|
| | Radium Cal | Bluephase G2 |
| CQ | 77.8 (6.8) aA | 77.3 (14.1) aA |
| CQ/PPD | 48.8 (7.4) bB | 71.6 (7.7) aA |
| CQ/BAPO | 31.5 (11.5) cB | 74.1 (6.9) aA |
| PPD | 47.2 (4.0) bB | 74.2 (6.4) aA |
| BAPO | 27.6 (3.9) cB | 81.6 (6.5) aA |

Means followed by different capital letters indicate statistically significant differences between curing lights for the same photoinitiator ($p < 0.05$). Means followed by different lower case letters indicate statistically significant differences among photoinitiator systems for the same curing light ($p < 0.05$).

The DC of an adhesive system is influenced by the activity of photoinitiators and the wavelength and intensity of the curing light that is applied¹⁹. In this study, only the adhesive systems that included CQ exhibited a similar DC between the samples that were photoactivated by Radium Cal and Bluephase G2. Conventional monowave LEDs, such as Radium Cal, have an emission band in the visible region which results in the emission of a single peak in a narrow spectral band²⁰. In contrast, Bluephase G2 is a dual peak LED that provides additional light with a spectrum that nearly includes 405 nm^{14,15}. CQ is activated within the visible light spectrum and has a peak absorbance near 470 nm^{6,7}. Based on the data collected, it appears that both monowave and polywave LEDs are able to excite CQ. This corroborates with that found by Segreto et al.²¹ (2016) who tested different photoinitiator units and photoinitiator systems and concluded that both types of light (mono and polywave) are capable of activating CQ and PPD.

Unlike CQ, the adhesive systems formulated with CQ/PPD, CQ/BAPO, PPD, and BAPO exhibited a higher DC when they were photoactivated by Bluephase G2 than with Radium Cal. Alternative photoinitiators such as PPD and BAPO have an absorption peak in the ultraviolet region (100–400 nm)²², specifically at 398 nm and 370 nm, respectively⁵. Thus, photoactivation with a polywave LED could promote an increased excitation of these photoinitiators, thereby increasing the generation of free radicals that initiate the polymerization reaction. However, the monowave LED, Radium Cal, provided a higher DC for the PPD adhesive system than the BAPO system. Thus, it is likely that PPD can also absorb light in the visible range of the light spectrum²⁰, thereby accounting for the greater excitation of PPD by Radium Cal compared with BAPO. The results indicated that PPD was a viable alternative in the formulation of experimental adhesives, observing that it presents greater reactivity independent of the type of photoinitiator unit²¹.

Despite the fact that BAPO is a Norrish Type I photoinitiator which generates free radicals via a photocleavage process that does not require a co-initiator²³, a tertiary amine EDMAB was added to the BAPO-containing materials in the present study. EDMAB is capable of reacting with the oxygen that is dissolved in the monomer, thereby reducing an oxygen-mediated inhibition of polymerization²³. Since CQ employs a mechanism that predominantly involves abstraction of a proton from the amine hydrogen, and PPD can undergo photocleavage and proton abstraction of the amine²⁴, EDMAB was included with all of the photoinitiators tested so the same conditions would be compared.

The findings obtained in this study are of great relevance, since DC is the main physical property related to other biological, physical and mechanical properties such as sorption and solubility, long-term stability of the hybrid layer²⁵, liberation of residual monomers and preservation of the complex dentin pulp⁴, bond strength to dentin⁹, elastic modulus and flexural strength of dental adhesives²⁶. Confirming this statement, Schneider et al.²⁷ (2009) evaluated the effect of the photoinitiator type on the maximum rate of polymerization ($R(p)(max)$), stress development (final stress and maximum rate, $R(stress)(max)$), DC and cross-link density (CLD) of materials containing CQ, PPD or CQ/PPD and conclude that CQ/PPD reduced the $R(p)(max)$ and $R(stress)(max)$ without a reduction in DC and CLD. In this way, 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.

Thus, to be able to show that the insertion of alternative photoinitiators in conjunction with third generation LEDs are able to increase the degree of conversion is a positive and relevant result for adhesive dentistry. The literature states, therefore, that the combination of alternative photoinitiators with the traditional camphorquinone/amine system improved the color stability of the model resin composites and maintaining their mechanical properties^{28,29}.

Despite the important finding obtained in this study regarding DC, further physical, mechanical and biological properties should be investigated to strength the effect of alternative photoinitiators on the performance of dental adhesives. Indeed, since acidic monomers such as methacryloyloxydecyl hydrogen phosphate (MDP), and glycerol dimethacrylate phosphate (GDMA-P) have been included in dental adhesive systems with Bis-GMA and/or HEMA^{30,31} further studies should be conducted to evaluate the DC exhibited by other formulations including acidic monomers and alternative photoinitiators.

In conclusion, the use of alternative photoinitiators and polywave LED was found to improve the DC and decrease the yellowing effect of the experimental dental adhesive systems tested.

Acknowledgements

This study was not supported by any funding agency. All expenses were made through own initiative.

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