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Mapping camphorquinone consumption, conversion and mechanical properties in methacrylates with systematically varied CQ/amine compositions

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ABSTRACT

Objectives. To evaluate conversion, bulk mechanical properties and camphorquinone (CQ) consumption in methacrylate resins, comprising a range of overall initiator concentrations and CQ/amine ratios.

Methods. BisGMA (Bisphenol-A glycidyl dimethacrylate), TEGDMA (triethyleneglycol dimethacrylate) and UDMA (urethane dimethacrylate) were mixed at a 1:1:1 molar ratio. CQ was used as the visible light photosensitizer, in combination with EDMAB (Ethyl p-dimethylamino benzoate), at 3:1, 2:1, 1:1, 1:2 and 1:3 weight ratios, at 0.5, 1.0, 1.5, 2.0 and 3.0 wt% overall initiator concentration. Butylhydroxytoluene was added at 0.05 wt% as an inhibitor. Unfilled resins were photoactivated with a dental light source (VIP Jr, Bisco) for 60 s at 600 mW/cm^2. Flexural strength/modulus were assessed in 2 × 1 × 10 mm bars, tested in three-point bending. Degree of conversion was assessed at the bottom of the same specimens using FT-RAMAN. CQ consumption was measured using a UV–vis spectrometer. Data were analyzed with two-way ANOVA/Tukey test ($\alpha = 5\%$).

Results. Lower conversion and inferior mechanical properties were observed with lower overall initiator concentrations and higher amine/CQ ratios. The lowest overall initiator concentration (0.5%) presented the statistically lowest conversion/properties results, except for the 1:3 amine/CQ ratio. For overall concentrations equal or greater to 1.5%, the amine/CQ ratio did not influence conversion or mechanical properties. CQ consumption was less efficient for the highest overall initiator concentrations and lower amine/CQ ratios.

Clinical relevance. Above 1.5 wt% overall initiator concentration, the conversion and general mechanical properties were independent of the initiator concentration. Therefore, there seems to be no benefit to increasing the initiator concentration above that level. At

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higher camphorquinone concentrations, light transmission and photosensitizer consumption becomes impaired, which could lead to decreased depth of cure and yellowing of the restoration.

1. Introduction

Camphorquinone (CQ) has been the most commonly used photosensitizer in direct restorative dental materials since UV was replaced by visible light initiation in the mid 70's due to biological concerns [1]. The first few research investigations in the area highlighted the poor light penetration of the now longer wavelengths and the somewhat inefficient quantum yield of camphorquinone [2]. Such inefficiency brings the need for relatively high concentrations of the photosensitizer to be used [3], as well as the addition of a co-initiator, most commonly a tertiary amine [2]. Current concerns still include discoloration effects, both from CQ's yellow color, but also from the potential oxidation over time of the co-initiator [4]. More recently, the use of alternative, color-stable photosensitizers has been proposed, with maximum absorbencies at the near UV (closer to 400 nm). The use of such initiators, however, made it necessary for modifications to be implemented in the current dental light curing units, to include the wavelengths of interest in their output spectral profile.

The concentration of initiators not only influences color and color stability, but it also directly correlates with fundamental properties of dimethacrylate resins [5]. Due to a phenomenon known as the inner shielding effect, excessive concentrations of the chromophore CQ may behave similarly to a bandpass filter, keeping the light from reaching deeper portions of the restoration [6,7], which is even more crucial when the already low average light penetration at 470 nm for conventional dental photopolymerization units is considered [8,9]. It has been recently reported that overall initiator concentrations greater than 1.4 wt%, with a 1:0.4 mol% CQ/amine ratio, did not further improve the degree of conversion or hardness on the bottom of 2 mm deep composite discs [5]. On the other hand, concentrations lower than 0.6 wt% produced degrees of conversion and hardness results 50% lower than with the optimized formulations [5]. Therefore, for a given monomeric system, it is important to consider not only the overall concentration of the initiator, but also the ratio between the two or more components in the initiator system.

It is noteworthy that the interaction between the light source also plays a major role, and parameters such as the light intensity at the critical wavelength also need to be considered [10]. Analogous to what is observed for excessively high initiator concentrations, the reciprocity between light intensity and exposure time does not always hold true [11], which means, in other words, that general properties and conversion may not benefit from higher light intensities, especially if the exposure time is short. That way, optimizations in the initiator concentration must be viewed in relation to the irradiation conditions being used.

While a good correlation between hardness and conversion is expected [12], being essentially a surface property, the hardness of a material is only able to provide limited information about network formation and other bulk mechanical properties. It has been demonstrated that greater conversion in dental composites increases fracture toughness [13,14], flexural properties [15,16] and resistance to degradation [17]. For those studies, the variations in conversion were achieved by using different photoactivation protocols. When the initiator concentration is varied with the same purpose, a threshold in conversion and mechanical properties improvement is observed above a certain concentration [18,19], and little consideration is given to the effects of unreacted initiators that were added in excess. Moreover, most of the studies use either a fixed CQ/amine ratio and vary the overall initiator concentration [18,19] or keep the overall initiator concentration constant and vary the ratio of the components [5]. A more systematic approach analyzing the influence of both the overall initiator concentration and the ratio of the components on bulk mechanical properties is lacking.

Ultimately, a simpler approach to reduce yellowing and discoloration over time would be to optimize both the concentration and the ratio of CQ/amine to ideally lead to the complete consumption of all the initiators in the polymerization, and still produce polymers with good physical properties. Therefore, this study proposes to evaluate conversion and bulk mechanical properties, as well as CQ consumption, of a series of model compositions of CQ/amine, comprising a range of overall initiator concentrations and CQ/amine ratios. We hypothesize that (1) properties and conversion will improve with higher initiator concentrations and (2) properties and conversion will be affected by the ratio CQ/amine.

2. Methods and materials

2.1. *Materials formulation*

All materials were used as received. Monomers were donated by ESSTECH (Essington, PA, USA) and initiators and inhibitors were purchased from Sigma–Aldrich (Milwaukee, WI, USA). BisGMA (Bisphenol A glycidyl dimethacrylate), TEGDMA (triethylene glycol dimethacrylate) and UDMA (urethane dimethacrylate) were mixed at a 1:1:1 molar ratio. Camphorquinone (CQ) was used as the visible light photosensitizer, in combination with EDMAB (Ethyl p-dimethylamino benzoate), at 3:1, 2:1, 1:1, 1:2 and 1:3 weight ratios, at 0.5, 1.0, 1.5, 2.0 and 3.0 wt% overall initiator concentration. To all 25 resulting mixtures, BHT (Butylhydroxytoluene) was added at 0.05 wt% as a radical inhibitor. No filler was added.

2.2. Mechanical properties

Flexural properties were evaluated in bar shaped specimens (10 × 1 × 2 mm) made in silicone molds, by sandwiching the resin materials between glass slides ($n = 10$). Specimens were polymerized through a mylar strip with a single, 60 s exposure, using a quartz-tungsten-halogen dental light (VIP Junior, Bisco, Schaumburg, IL, USA) at 600 mW/cm^2, equipped with a light guide with 11 mm in diameter, and stored dry for 24 h at room temperature in opaque containers before being tested in three-point bending (Instron, Canton, MA) at a cross-head speed of 0.5 mm/min until failure. The irradiated side of the specimen (top) was positioned opposite from the load application point (under tensile stress). Flexural strength (FS, in MPa) and flexural modulus (FM, in GPa) were calculated according to the following equations:

$$FM = \frac{L_1 \times D^3}{4 \times w \times h^3 \times d} \times 10^{-3} \qquad FS = \frac{3 \times L \times D}{2 \times w \times h^2}$$

where L = failure load (N), D = spam between supports (8 mm), w = width (mm) and h = thickness (mm) and d = crosshead displacement (mm).

2.3. Degree of conversion

Degree of conversion (DC, $n = 3$) was determined by FT-Raman spectroscopy (Bruker Inc., Woodlands, TX, USA) on the irradiated (top) surface of fragments retrieved from flexural strength immediately after the mechanical test. Spectra were obtained by the co-addition of 64 scans at a resolution of 4 cm^{-1}. Vinyl conversion was determined based on the absorption band at 1638 cm^{-1}, using the aromatic band at 1610 cm^{-1} as an internal reference. Spectra were collected for the polymerized and unpolymerized material, and conversion was calculated as follows:

$$DC = \left(\frac{(\text{vinyl/aromatic})_{\text{polymerized}}}{(\text{vinyl/aromatic})_{\text{unpolymerized}}} \right) \times 100$$

where DC is the degree of conversion, vinyl is the area under the 1638 cm^{-1} band, aromatic is the area under the 1610 cm^{-1} band for the polymerized and unpolymerized material.

2.4. Light attenuation calculation (thin film approximation)

Since camphorquinone absorbs light, a theoretical calculation of the light attenuation in depth was carried out using thin film approximation [20,21] (assuming 1 mm thick specimens), according to the following formula:

$$I\prime = I_0 10^{(-\varepsilon D [A])}$$

where: I' = irradiance at depth D (cm); I_0 = incident irradiance. ε = camphorquinone molar absorptivity (46 L/mol cm). [A] = camphorquinone concentration (mol/L).

The densities of the samples were accounted for in the calculation of the molar concentration of initiators, which was then used to calculate light attenuation.

2.5. UV–vis experiments

The decrease in camphorquinone absorption at 470 nm reflects its consumption in the polymerization initiaton. The absorption at 470 nm was followed using a UV–vis spectrometer (Evolution 201, ThermoScientific, Milwaukee, WI) in specimens polymerized inside UV-transparent cuvettes (1 mm path length, approximately 0.5 g of resin) and ratioed against the absorption of the same specimens prior to light exposure to give the percentage camphorquinone consumption after polymerization. Neat resins (no initiator added) were used as the background.

2.6. Statistical analysis

Data were submitted to two-way ANOVA and Tukey test. A preset global significance level of 5% was adopted for all analyses.

3. Results

Conversion results ranged from 40 to 80% (Fig. 1A). In general, a trend was observed for lower conversion with lower total initiator concentrations and higher amine/CQ ratios. The lowest total initiator concentration (0.5%) presented the statistically lowest conversion results, except for the 1:3 amine/CQ ratio. For 1.0% overall initiator concentration, only the 3:1 ratio was statistically lower than the others in its group. For total concentrations equal or greater to 1.5%, the amine/CQ ratio did not significantly influence conversion. Flexural strength (Fig. 1B) and modulus (Fig. 1C) increased with increasing total photoinitiator concentrations for all amine/CQ ratios. Within the same total concentration, the effects of amine/CQ ratio on flexural properties were not as pronounced as what was observed for conversion. In general, for a given concentration, the flexural strength and modulus presented in a narrow range irrespective of the ratio of amine/CQ. For flexural modulus, the total initiator concentration of 0.5 wt% presented statistically lower results than any other concentration, at all ratios. At 1.0 wt%, the flexural modulus was dependent on the amine/CQ ratio, with 2:1, 1:1 and 1:3 showing statistically better results. Above 2.0 wt% total initiator concentration, all values were statistically similar ($p > 0.05$). For flexural strength, the same trends were observed, except that the concentration needed for the mechanical property to be independent of the amine/CQ ratio was 3.0 wt%. At 2.0 wt%, statistically higher results were observed with amine/CQ ratios of 1:1, 1:3 and 3:1.

The UV–vis test showed three ranges of CQ consumption, as denoted by the different regions on Fig. 2A. The general trend was that CQ consumption was higher for the lower total initiator concentrations and higher amine/CQ ratios, as expected. At the higher total initiator concentrations and lower amine/CQ ratios, only 15–28% of the camphorquinone was consumed in the polymerization reaction. The same three ranges were observed when the light attenuation due to inner shielding of CQ was calculated using thin film approximation (Fig. 2B). Again, the least attenuation was observed for the lower total initiator concentrations and higher amine/CQ ratios.

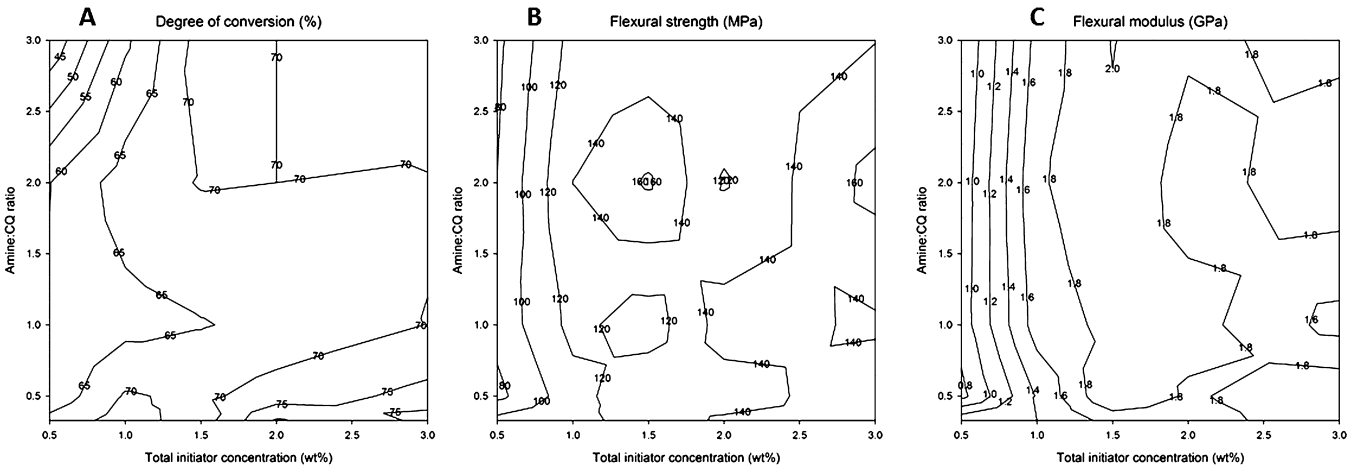

Fig. 1 – Contour plot for (A) degree of conversion (%), (B) flexural strength (MPa) and (C) flexural modulus (GPa) for the different formulations.

4. Discussion

With the experimental design proposed in this study, gradient maps were produced for conversion, mechanical properties, theoretical light attenuation and CQ consumption. As expected, based on the direct dependency between those variables, all maps followed the same general trend, *i.e.*, higher conversion/better mechanical properties (Fig. 1), and less CQ consumption/greater light attenuation for higher total initiator concentrations and lower amine/CQ ratios (Fig. 2).

When the highest total initiator concentration is considered, the variation in conversion results among the different amine/CQ ratios is only within 16% (from 60 to 76%). The same is true for the intermediate concentrations (1 through 2%). However, when the overall initiator concentration drops to 0.5%, higher amine/CQ ratios lead to conversion variations of around 26% (between 40 and 66%). This means that at lower initiator concentrations the inefficiency of CQ as a photosensitizer is highlighted, and greater concentrations are necessary to increase the quantum yield conversion. More specifically for the extreme of 0.5% initiators, 3:1 amine:CQ translates into 0.125 wt% CQ, while the 1:3 ration translates into 0.375 wt% CQ. That increase in CQ concentration corresponded to an increase in conversion of 26%. However, the consumption of CQ (Fig. 2A) was one of the lowest, with almost 79% of the initial concentration left non-reacted. There are two explanations for the decreased efficiency of CQ. The first is evidenced

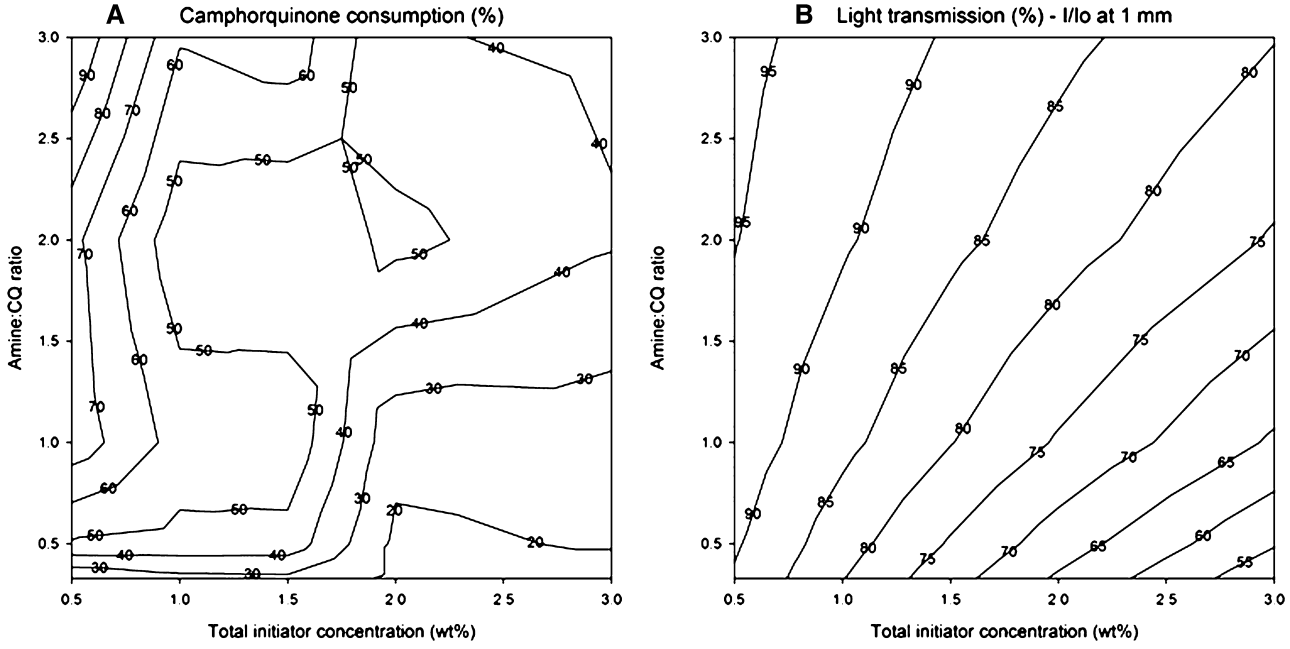

Fig. 2 – Contour plot for (A) camphorquinone consumption as assessed by percentage drop in absorption at 470 nm obtained with UV–vis experiments (%) and (B) percentage light transmission prediction through a 1 mm thick resin film for the different formulations.

by the decrease in light transmission with that formulation given by the high concentration of unused CQ, working as a shield to light penetration (Fig. 2B), as previously reported [6,22]. The second lies in the fact that at the same time the CQ concentration increases, the amine concentration decreases. An interesting analysis is the comparison between increasing CQ concentrations for the same amine concentration (which is accomplished by comparing different overall initiator concentrations). For example, when the amine concentration is 0.75 wt% (which happens for 1 wt% initiators, at 3:1 amine:CQ; for 1.5 wt% initiators, at 1:1 amine:CQ and for 3 wt%, at 1:3 amine:CQ), increasing the CQ concentration from 0.25 wt% to 0.75 wt% and then to 2.25 wt% leads to conversion values of 59, 65 and 72%, respectively. This is explained by the greater likelihood of a photon encountering a photosensitizer molecule to interact and initiate conversion. It is noteworthy that the CQ consumption for those same concentrations decreased appreciably with increased CQ concentration: 61, 58 and 16% of the initial CQ was used up in the reaction, as denoted by the UV–vis experiments, shown in Fig. 2A. That adds evidence to the very inefficient use of CQ as a photosensitizer, and explains why a ratio amine/CQ greater than the theoretically expected (2:1, based on the number of potentially generated radicals) is necessary to optimize properties, as will be discussed later. Conversely, when the CQ concentration is 0.75 wt% (which happens for 1 wt% initiators, at 1:3 amine:CQ; for 1.5 wt% initiators, at 1:1 amine:CQ and for 3 wt%, at 3:1 amine:CQ), increasing the amine concentration from 0.25 wt% to 0.75 wt% and then to 2.25 wt% leads to conversion values of 75, 65 and 72%, respectively. This means that the CQ concentration is the limiting factor to conversion at that concentration.

In more general terms, the threshold concentration/ratio above which no significant increase in conversion was gained was observed above 1.5% for the highest amine/CQ ratios, which agrees with previously reported data [5]. However, as the amine/CQ ratio decreased, the overall initiator concentration had to be higher for comparable values of conversion to be achieved (Fig. 1). This stems from CQ's low efficiency, and there is limited benefit of adding excess amine to the mixture to allow for the overall concentration of CQ to be lowered. At a 3:1 amine/CQ ratio, the overall concentration had to be increased to 1.5% for 65% conversion to be achieved, a result that was obtained for the inverse ratio (1:3) at only 0.5% initiator concentration (higher absolute CQ concentration). However, the poor CQ consumption for the latter is a concern, as discussed later in the text.

Compared to the conversion results, mechanical properties were less markedly influenced by the ratio of initiators, and above 1.5 wt%, all groups essentially reached similar values of flexural modulus (Fig. 1), and above 1.0 wt%, all groups presented similar flexural strength (Fig. 1). Because flexural strength and modulus reflect bulk properties of the material, it is not surprising that above a certain threshold of conversion no additional increments in mechanical properties were observed. In more detail, at the lowest initiator concentration, in spite of the 90–96% light transmission through the sample, it is likely that not enough initiation centers were activated upon irradiation. This is consistent with gelation at lower values of conversion, which in turn impairs final conversion, also likely leading to less crosslinked networks [23,24]. On the other hand, the fact that CQ consumption drops dramatically above 2 wt% initiator concentration, especially for the lowest amine/CQ ratios (1:3), explains the similar results in flexural properties even with increasing initiator concentrations beyond the 2 wt% level. In addition, the excess CQ left in the bulk of the material acts as a filter impairing light penetration, in an effect known as inner shielding [22,25]. In fact, the lowest value of light transmission was recorded for the material with the highest initiator concentration, with the lowest amine/CQ ratio (the highest nominal CQ concentration).

In conclusion, this study demonstrated that conversion is more affected by the initiator system composition and concentration than bulk mechanical properties. Above 1.5 wt% overall initiator concentration, the conversion and general mechanical properties were independent of the initiator concentration. Therefore, there seems to be no benefit to increasing the initiator concentration above that level. On the contrary, as evidenced by the increased light attenuation and decrease camphorquinone consumption at higher initiator concentrations, especially for the groups where a higher proportion of CQ was used, there may be a risk for yellowing of the restoration short- and long-term, as well as toxic effects (not evaluated here), due to unreacted initiator species. Within the limitations of this study, the present results suggest that overall initiator concentrations of 1.5 wt% at a amine/CQ ratio of 3:1 presented the best compromise among CQ consumption, light attenuation, degree of conversion and mechanical properties.

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