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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 $2 \times 1 \times 10$ 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.