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Quantum yield of conversion of the photoinitiator camphorquinone

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ABSTRACT

The primary absorber in dental resins is the photoinitiator, which starts the photo polymerization process. We studied the quantum yield of conversion of camphorquinone (CQ), a blue light photoinitiator, in dental resin composites using a LED lamp (3M FreeLight) and a Quartz Tungsten Halogen (QTH) lamp (VIP) as the light curing units at five different irradiances. The molar extinction coefficient, ε_{469}, of CQ was $46 \pm 2\,\text{cm}^{-1}/(\text{mol/L})$ at 469 nm. The reciprocity of irradiance and exposure time holds for changes of CQ absorption coefficient, that is, irradiance × exposure time (=radiant exposure) = constant. Both LED and QTH lamps yielded the same curing threshold (the radiant exposure when CQ absorption drops to 1/e) and the same quantum yield conversion under different irradiances. In our dental resin formulation (0.7 wt.% CQ with reducing agents 0.35 wt.% dimethylaminoethyl methacrylate (DMAEMA) and 0.05 wt.% butylated hydroxytoluene (BHT)) the quantum yield was measured as 0.07 ± 0.01 CQ conversion per absorbed photon.

1. Introduction

Photo-cured composites are widely used in dental restorations due to their many advantages, including the esthetic appearance and the ability to cure *in situ*. However, limited light transport in the composite and insufficient extent of cure may compromise the physical properties of the composite and reduce its service life. These composites consist of a mixture of resins with photoinitiators and silane-coated, inorganic filler particles. The component that absorbs light and initiates free radical addition polymerization of the resin monomers is the photoinitiator. The number of the photoinitiators should be limited to a concentration that is just sufficient to obtain an optimum photocuring reaction with the highest possible monomer conversion because any excessive unreacted photoinitiators, products of their photolysis, or any unreacted monomers, may diffuse out from the polymer matrix into the saliva. On the other hand, to avoid leaving unreacted photoinitiators also requires a sufficient amount of light application. In order to know the required light dose that will completely convert all of the photoinitiators, we need to know the photoinitiator quantum yield conversion, which is defined as the ratio of the number of converted photoinitiators to the number of photons absorbed by the initiators:

$$\Phi = \frac{\text{number of converted photoinitiator molecules}}{\text{number of absorbed photons}}. \quad (1)$$

The most commonly used photoinitiator in dental resin formulations is camphorquinone (CQ), a blue light photoinitia-

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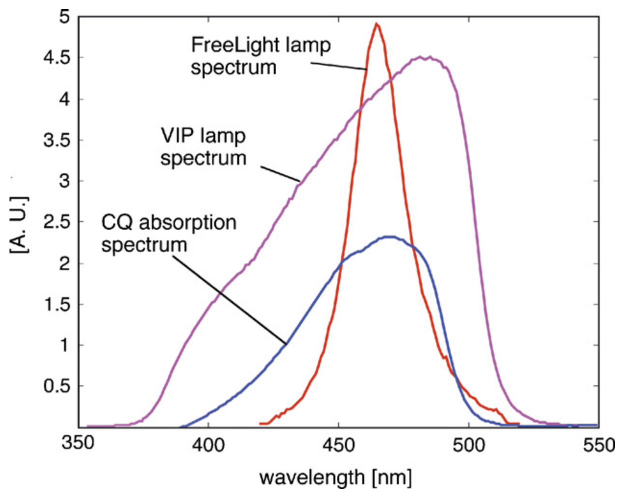

Fig. 1 – Comparison of the spectra of the 3M FreeLight LED light curing unit, VIP lamp, and CQ absorption. The peak of the spectrum is at 465 nm for 3M lamp, 482 nm for VIP lamp, and 469 nm for absorption by CQ.

tor [1]. CQ, a di-2,3-diketo-1,7,7-trimethylnorcamphane, has a molecular weight of 166 and an absorption peak around 469 nm (Fig. 1). Some research has focused on the mechanism of the free radical polymerization process photoinitiated by CQ in the TEGDMA polymer system [2–5], and demonstrated photochemical reactions between CQ and various coinitiators or the monomers in different environments (i.e. air or N_2). Little work has been done on the relationship between the amount of light and the CQ conversion. Monroe and Weiner studied the photoreduction mechanism and the quantum yield for disappearance of CQ in methanol and isopropyl alcohol solutions [6]. In this study, we attempted to construct a general principle of how the measurements can be performed and to detail how the quantum yield conversion can be calculated. We investigated the quantum yield conversion of CQ in dental resin composites using the light sources, which are commercially available and widely used by dentists.

Not all the photons delivered to the composite are absorbed. Only those photons that are absorbed by the photoinitiators can possibly cause photopolymerization. Therefore, it is the effective absorbed power density (irradiance × absorption coefficient), not just the irradiance of the lamp, that influences polymerization. Some studies [7,8] suggested a "integrated relative curing potential" (ICP_{rel}) parameter defined as the integration of the product of the spectral irradiance of the curing unit (at each wavelength) with the relative absorbance of photoinitiator (at the same wavelength) over all the wavelengths emitted by the lamp. That is:

$$ICP_{rel} = \int_{\lambda_1}^{\lambda_2} E(\lambda)A(\lambda)\,d\lambda, \quad (2)$$

where $E(\lambda)$ is the spectral irradiance of the curing unit, $A(\lambda)$ the relative absorbance of photoinitiator, and λ_1 to λ_2 the wavelength emission range of the curing unit. If $A(\lambda)$ is replaced by the absorption coefficient $\mu_a(\lambda)$ of the photoinitiator, instead of representing the "relative" curing potential, the parameter gives the effective value of the total absorbed energy per unit volume in the material (according to the CIE/ISO definition [9]):

$$E_{abs} = \int_{\lambda_1}^{\lambda_2} E(\lambda)\mu_a(\lambda)\,d\lambda. \quad (3)$$

This value decreases as the absorption coefficient decreases during curing.

Our previous study showed that the absorption of the commercial dental composite Z100 decreases during the curing process, especially around CQs absorption peak, 470 ± 10 nm [10]. This implies that the major component causing the change in absorption is the photoinitiator, CQ. This study attempted to study the relationship between the conversion of CQ and the amount of light absorbed by CQ. In our previous study, we found a reciprocal relationship between the irradiance (E_a) and exposure time (t), that is $E_a t$ = constant, for the degree of conversion and the hardness accretion of the Z100. Based on these observations, we hypothesized that the reciprocity of irradiance and exposure time also holds for the conversion of the photoinitiator CQ. In other words, given the same radiant exposure (irradiance × exposure time = radiant exposure), we should get the same number of photoinitiator conversions. In this study, we delivered five different irradiances by using two different commercially available dental curing lamps (FreeLight LED and VIP) to cure dental composite resins (containing 0.7 wt.% of CQ). We used two different methods to measure the absorption changes of CQ and the total absorbed photons to compromise the advantages and disadvantages of each method. The CQ extinction coefficient was also measured to relate the absorption coefficient with the number of remaining CQ molecules. Combining the information of the total number of converted CQ molecules as a function of time and the total number of absorbed photons as a function of time, we were able to quantify the quantum yield of CQ conversion (Eq. (1)). Moreover, based on the reciprocity of irradiance and exposure time, the radiant exposure threshold ($H_{50\%}$) for 50% of CQ conversion was determined.

2. Materials and methods

2.1. Materials

The resin formulation used for this study was 50:50 weight ratio of 2,2-bis[4-(2-hydroxy-3-methacryloyloxypropoxy)-phenyl]propane (BIS-GMA) to triethyleneglycol dimethacrylate (TEGDMA) (Esstech, Essington, PA), with 0.35 wt.% dimethylaminoethyl methacrylate (DMAEMA) (Alfa, Ward Hill, MA, USA), and 0.05 wt.% butylated hydroxytoluene (BHT) (Alfa, Ward Hill, MA, USA) inhibitor (without photosensitizer). For resins with photosensitizer, up to 0.7 wt.% of camphorquinone (CQ) (Alfa, Ward Hill, MA, USA) was added.

2.2. CQ absorption versus CQ concentration

To measure the absorption coefficient as a function of CQ concentration, 4 mm thick cuvettes were filled with resin solutions with five different CQ concentrations (0, 0.26, 0.35, 0.52, and 0.7 wt.%) and were covered with aluminum foil to