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Quantum yield of conversion of the photoinitiator camphorquinone

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ARTICLE INFO

Article history:

Received 24 November 2005

Received in revised form

22 May 2006

Accepted 9 June 2006

Keywords:

Dynamic absorption coefficient

Light-activated polymerization

Molar extinction coefficient

Curing threshold

Reciprocity

Radiant exposure

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 \times 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.

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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 pho-

toinitiators, 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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doi:10.1016/j.dental.2006.06.005

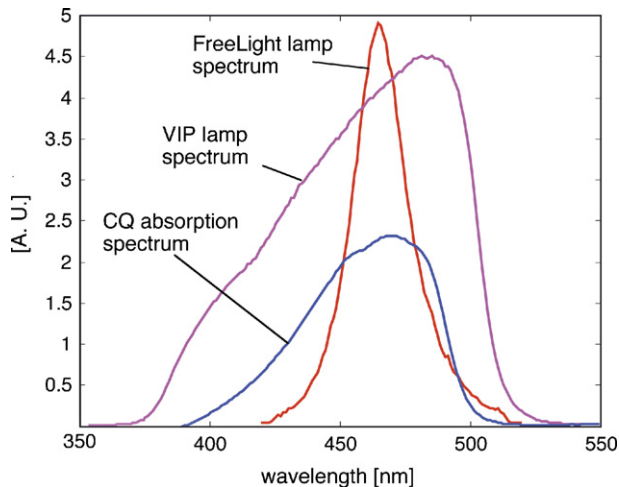


Fig. 1 – Comparison of the spectra of the 3M FreeLight LED light curing unit, VIP lamp, and CQ absorption. The peak of the spectrum is at 465 nm for 3M lamp, 482 nm for VIP lamp, and 469 nm for absorption by CQ.

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 N₂). 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:

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

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]):

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

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 $E_a t = \text{constant}$, 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

avoid premature photo-activation. The absorbance of the samples was measured with a Cary 100 Bio Spectrophotometer (Varian Scientific Instruments Inc., Walnut Creek, CA) scanning from 550 down to 400 nm. This spectrophotometer is a differential system: differences in absorption of the sample and of the reference material are measured. A 4 mm cuvette filled with water was used as the reference material for these measurements.

2.3. CQ absorption versus radiant exposure

Two different methods were used to measure the absorption changes as a function of radiant exposure and to quantify the number of photons absorbed by the CQ molecules. First, we used the spectrophotometer to measure the CQ absorption spectrum as a function of curing time. From those spectra, we calculated the total absorbed photons as a function of time using Eq. (3). The second method used an Ocean Optics spectrometer as the detector, which recorded the transmitted light spectrum passed through the resins. The absorbed light spectrum was calculated by directly subtracting the original lamp spectrum by the transmitted light spectrum. In this method, the measured light source and the curing light source were the same. This helped to confirm whether the first method had an artificial effect by using two different light sources. However, the second method had the disadvantage of fluctuating irradiance (~5%) of the curing light source (the VIP lamp).

2.3.1. Method I—absorption spectrum method

We used the Cary spectrophotometer to measure the absorption coefficient of resin with 0.7% CQ as a function of illumination time for three irradiances. A LED lamp (FreeLight, 3M ESPE, Seefeld, Germany) with a 7 mm diameter illumination tip was chosen as the light curing unit. The LED lamp has an illumination peak at 465 nm with narrow bandwidth (FWHM = 24 nm). This emission profile is close to the spectral absorption of CQ (Fig. 1). The spectrum of the lamp was measured using a spectrofluorometer (SPEX Fluorolog-3, Jobin Yvon Inc., Edison, NJ, USA). The total power of the lamp was 135 ± 1 mW, measured with a power meter (S210A/M, Thorlabs Inc., Newton, NJ). To vary the curing irradiance, the LED was placed at three different distances, 10, 15, and 27 mm, away from the surface of the sample. The corresponding irradiances E_{total} were derived in Section 3 and summarized in Table 1. The battery of the LED lamp was fully charged before each irradiance measurement.

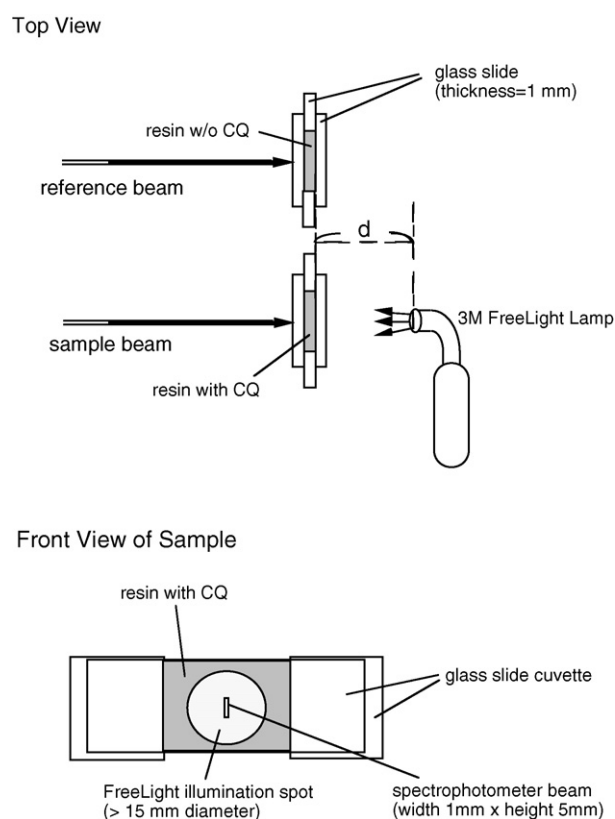


Fig. 2 – Experimental setup for dynamic absorption measurements. The top picture is a top view of the chamber of the spectrophotometer. Resin without CQ was placed at the reference arm and resin with CQ was in the sample arm. The samples were in glass-slide cuvettes with a thickness of 1 mm. The LED lamp (FreeLight) was placed in front of the sample arm at distance $d = 10, 15,$ or 27 mm to irradiate the CQ resin sample. The bottom picture is a front view of the CQ resin sample. The beam in the spectrophotometer is 1 mm wide and 5 mm high, at the center of the LED illumination spot.

The experimental setup inside the Cary spectrophotometer chamber is shown in Fig. 2. Approximately 0.5 cm^3 of resin was filled into a custom-made glass-slide cuvette with thickness of 0.95 ± 0.05 mm. The sample arm was resin with 0.7% CQ (called

Table 1 – List of values and their standard deviations

	w (cm) ± 0.05	E_{total} (mW/cm ²) $\pm 10\%$	μ_{ao} (cm ⁻¹) ± 0.01	τ (s) $\pm 1\%$	τE_{total} (mJ/cm ²) $\pm 11\%$	$\tau \sqrt{E_{\text{total}}}$	$\Phi \pm 11\%$
LED#1	0.5	160	4.41	280	44800	3540	0.07
LED#2	0.7	90	4.51	525	47250	4980	0.07
LED#3	1.2	30	4.46	1385	41550	7586	0.07
	w (cm) ± 0.02	E_{total} (mW/cm ²) $\pm 5\%$	μ_{ao} (cm ⁻¹) ± 0.1	τ (s) $\pm 5\%$	τE_{total} (mJ/cm ²) $\pm 11\%$	$\tau \sqrt{E_{\text{total}}}$	$\Phi \pm 11\%$
QTH#1	0.5	345	5.9	120	41400	2230	0.09
QTH#2	0.5	95	4.8	435	41325	4240	0.07

w is the radius of the lamp illumination spot in Eq. (12). The P_{total} is 135 mW for the LED lamp, and 74 and 270 mW for the QTH lamp#1 and #2. μ_{ao} and τ are the fitting parameters of the exponential model (Eq. (13)). Φ is the calculated quantum yield from each experiment.

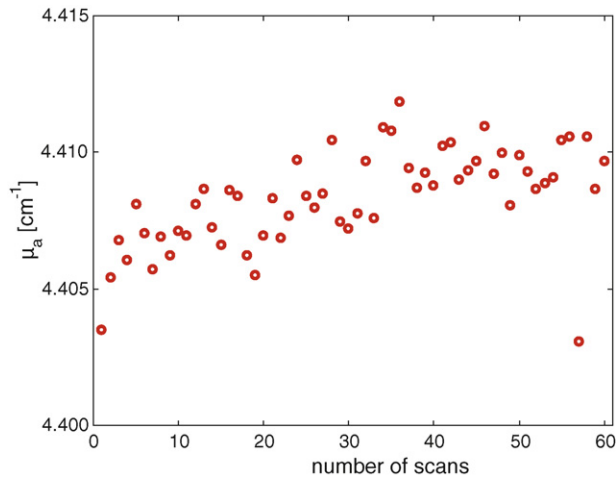


Fig. 3 – The absorption coefficient μ_a at wavelength 469 ± 1 nm over the 60 scans with the Cary spectrophotometer. Note that the scale in y-axis is from 4.400 to 4.415 cm^{-1} .

“CQ resin”). The reference arm was resin without CQ. Since the molar extinction coefficient of CQ is about $4.6 \times 10^4 \text{ cm}^2 \text{ mol}^{-1}$ (see Section 4, Fig. 5), a film of this thickness with 0.7% of CQ resulted in about 35% (maximum) variation in irradiance across the thickness of the film.

The power of the spectrophotometer beam was lower than the detection limit, $0.1 \mu\text{W}$, of the power meter (LiCONiX 45PM Power Meter, Nolatek, Houma, LA). Therefore the radiant exposure for each scan was $<0.1 \mu\text{J}/\text{cm}^2$. To evaluate the potential curing effect from the spectrophotometer beam, the scan from 550 to 400 nm was repeated 60 times sequentially (CQ resin at the sample arm and resin without CQ at the reference arm) without any other light source on. The standard deviation of the spectrophotometer absorbance measurements is about 0.002 cm^{-1} (Fig. 3). The absorption coefficient at 469 nm increased from 4.405 to 4.410 cm^{-1} over the 60 time sequential scans. This $\sim 0.1\%$ change is significant (ANOVA: $p < 0.01$), but is negligible comparing to the absorption changes caused by the LED illumination (see Fig. 8) (e.g. μ_{a469} dropped 20% for the first 60 scans at irradiance $30 \text{ mW}/\text{cm}^2$).

The irradiance across the LED lamp illumination spot (approximately 15 mm in diameter or larger) was found to be a Gaussian distribution. Therefore, the absorbance across this spot might not be uniform. To decrease this non-uniform effect, we made measurements only within the center of the spot. To do this, we blocked half of the spectrophotometer beam (original width by height = $1 \text{ mm} \times 10 \text{ mm}$) in both channels so that only a rectangular $1 \text{ mm} \times 5 \text{ mm}$ of beam reached the samples. According to our irradiance measurement, the LED lamp irradiance deviation across that 5 mm height was less than 15% (for the lamp tip positioned 10 mm away from the sample).

The LED curing beam was aligned with the center of the spectrophotometer beam (Fig. 2). During the experiment, the positions of both glass-cuvette samples (the sample arm and reference arm) were fixed. This ensured that the spectrophotometer always detected the same spot of the samples. The

LED was moved into a curing position to irradiate the CQ resin sample and then moved away for the subsequent absorption measurement.

The absorbance scan was from 550 to 400 nm at a speed of $0.1 \text{ s}/\text{nm}$. The absorbance of the CQ resin was scanned before any curing began. After this, the sample was illuminated with the LED followed by a single absorbance scan (15 s). The curing/absorbance scan process was repeated until changes in absorbance were negligible. The LED illumination was 2 s followed by an absorbance scan for the first 10 measurements, 5 s for the next 24 measurements, 10 s for the next 10 measurements, 20 s for the next eight measurements, 30 s for the next eight measurements, and every 40 s for the rest of the time.

The measured absorbance $A(\lambda)$ at wavelength λ was calculated by using a moving average of the absorbance from $\lambda - 1$ to $\lambda + 1 \text{ nm}$. Since:

$$10^{-A(\lambda)} = \exp^{-\mu_a(\lambda)d}, \quad (4)$$

the absorption coefficient at wavelength λ is $\mu_a(\lambda) = A(\lambda)(\ln 10)/d$, where $d = 0.1 \text{ cm}$ is the thickness of the sample.

2.3.2. Method II—transmitted spectrum method

In this method, the transmitted light was recorded as a function of irradiation time. The experimental setup was shown in Fig. 4. We used a quartz tungsten halogen (QTH) lamp (VIP, Bisco Inc., Schaumburg, IL) as the light source and a spectrophotometer (S2000, Ocean Optics, Dunedin, FL, USA) as the detector. A Thorlabs power meter was used to measure the power for each of the six power settings in the lamp. The resin was filled in a glass-slide cuvette with a thickness of 1 mm. The QTH lamp was placed in front of the sample at distance $d \leq 1 \text{ mm}$ to irradiate the CQ resin sample. A $200 \mu\text{m}$ optical fiber was placed at the center of the illumination spot to collect the transmitted light. Note that, in this experiment, a continuous light source was needed because the transmitted light was recorded by the spectrophotometer in real time.

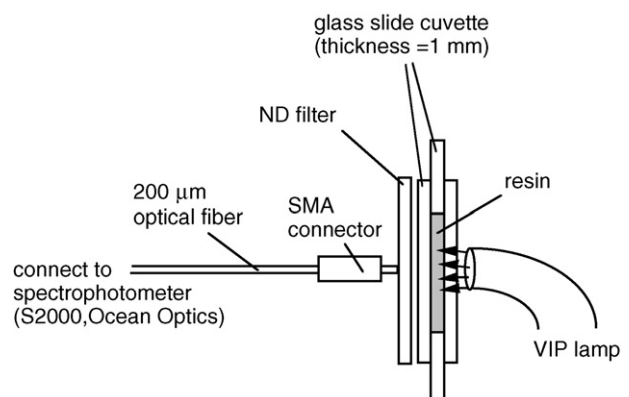


Fig. 4 – Schematic drawing of the experimental setup for transmitted spectrum method using a QTH lamp (VIP) as the light source and the Ocean Optics spectrometer as the detector. The resin was in a glass-slide cuvette with a thickness of 1 mm. The VIP lamp was placed in front of the sample at distance $d \leq 1 \text{ mm}$ to irradiate the CQ resin sample. A $200 \mu\text{m}$ optical fiber was placed at the center of the illumination spot to collect the transmitted light.

Therefore, the QTH lamp was chosen in this experiment as the operation time of this lamp allows for 250 s of illumination in a continuous mode (while the FreeLight LED lamp can only be activated for 40 s each time it is turned on).

Two powers (74 and 270 mW) were used for the measurements. Note that the power of the lamp fluctuates periodically over the 250 s cycle, however, the power is then stabilized (~5% fluctuation) approximately 20 s after it is turned on until about 240 s. Therefore, the powers stated here are the averaged power during the 20–240 s period. The corresponding irradiances E_{total} were derived in Section 3 and summarized in Table 1. For each power, the original lamp spectrum $E_0(\lambda)$ was measured by filling a glass-slide cuvette with resin without CQ. The transmitted light was collected every 20 s for a total of 10 spectra. Then, the cuvette was changed to a cuvette filled with CQ resin. The transmitted spectrum was recorded every 20 s for the first 600 s and every 30 s thereafter until the change in transmission was less than 5%.

The absorption coefficient was calculated as:

$$\mu_a(\lambda, t) = -\frac{1}{d} \ln \frac{T(\lambda, t)}{E_0(\lambda)}, \quad (5)$$

where d is the thickness of the sample, $T(\lambda, t)$ the transmitted light, and $E_0(\lambda)$ the incident light. The absorbed photon density (number of photons per unit volume), $Q(\lambda, t)$, can be calculated directly by subtracting the transmitted light from the incident light:

$$Q(\lambda, t) = \frac{\rho}{d} \frac{\lambda}{hc} (E_0(\lambda) - T(\lambda, t)), \quad (6)$$

where h is Planck's constant, c the speed of light, and ρ a constant to convert the spectrometer units (count) to the real lamp power (W) and can be determined by the ratio of the total "real" power to the total "measured" power:

$$\rho = \frac{\text{power}}{\int_{\lambda} E_0(\lambda)}, \quad (7)$$

where $\int_{\lambda} E_0(\lambda)$ is the integration of the lamp spectrum measured by the spectrometer. ρ here is a constant and wavelength independent.

3. Theory

3.1. Total irradiance of the curing illumination

The spectral power per nanometer of the wavelength λ of the lamp $P(\lambda)$ can be represented as:

$$P(\lambda) = P_{\text{total}} f(\lambda), \quad (8)$$

where P_{total} is the total power and $f(\lambda)$ the spectral probability distribution at wavelength λ , that is:

$$P_{\text{total}} = \int_0^{\infty} P(\lambda) d\lambda \quad \text{and} \quad \int_0^{\infty} f(\lambda) d\lambda = 1. \quad (9)$$

The spatial irradiance across the illumination spot has a Gaussian distribution with a radius w (where the irradiance

drops 1/e). If $E(\lambda, r)$ is the spectral irradiance at wavelength λ and at distance r from the center of the spot, then:

$$E(\lambda, r) = \frac{P(\lambda)}{\pi w^2} \exp\left(-\left(\frac{r^2}{w^2}\right)\right). \quad (10)$$

Therefore, the average irradiance at wavelength λ over a circle with a radius r_0 is:

$$E(\lambda, r_0) = \frac{1}{\pi r_0^2} \int_0^{r_0} E(\lambda, r) 2\pi r dr = \frac{P(\lambda)}{\pi r_0^2} \left(1 - \exp\left(-\frac{r_0^2}{w^2}\right)\right). \quad (11)$$

The total irradiance over the r_0 area is obtained by integrating over all wavelengths emitted by the lamp or:

$$E_{\text{total}}(r_0) = \frac{P_{\text{total}}}{\pi r_0^2} \left(1 - \exp\left(-\frac{r_0^2}{w^2}\right)\right). \quad (12)$$

In our experiment, the irradiances E_{total} were calculated using $r_0 = 0.25$ cm for the LED lamp and $r_0 = 0.01$ for the QTH lamp and were summarized in Table 1.

3.2. Relationship between CQs absorption and lamp's illumination time

The absorption coefficient as a function of illumination time can be modeled as an exponential function [11,12]:

$$\mu_a(\lambda, t) = \mu_{a0}(\lambda) \exp(-t/\tau), \quad (13)$$

where $\mu_{a0}(\lambda)$ and τ are the fitting parameters. Physically, $\mu_{a0}(\lambda)$ is the initial absorption coefficient at wavelength λ at $t=0$. The time constant τ depends on the spectral irradiance of the curing lamp and CQs quantum yield. For example, a high irradiance will cause the absorption of CQ to decline rapidly and therefore the process will have a short time constant. In our experiment, the fitting was conducted for a total of five irradiances as shown in Figs. 8 and 9 in Section 4. Note that in the fitting, the first three data points were not included due to the increase of absorption for the first three points. It was found that a higher irradiance corresponds to a shorter T and that the irradiance $\times \tau \approx \text{constant}$ (Table 1). Therefore, we can rewrite Eq. (13) as:

$$\mu_a(t) = \mu_{a0} \exp\left(-\frac{E_{\text{total}} t}{H_{\text{threshold}}}\right), \quad (14)$$

where $H_{\text{threshold}} = E_{\text{total}} \times \tau$ is the curing threshold (where CQs concentration drops to 1/e), and this value is independent of the irradiance of the lamp.

3.3. Number of photons absorbed by CQ

The number of photons delivered by the lamp per area per second as a function of wavelength $N_{\text{photon}}(\lambda, t)$ is:

$$N_{\text{photon}}(\lambda, t) = \frac{E(\lambda, t)}{h\nu} = \frac{\lambda E(\lambda, t)}{hc}, \quad (15)$$

where $E(\lambda)$ is the irradiance at wavelength λ , h is Planck's constant, ν is frequency of light, and c is speed of light. The number of photons $Q(\lambda, t)$ absorbed by CQ per volume per second, as described in Eq. (3), is:

$$Q(\lambda, t) = N_{\text{photon}}(\lambda, t) \int_0^d e^{-\mu_a(\lambda, t)x} dx$$

$$= \frac{N_{\text{photon}}(\lambda, t)}{d} (1 - e^{-\mu_a(\lambda, t)d}). \quad (16)$$

The accumulated number of photons, $A_{\text{photon}}(t)$, absorbed by CQ per volume at time t is equal to the sum of $Q(\lambda, t)$ over all wavelengths and from time 0 throughout time t :

$$A_{\text{photon}}(t) = \sum_0^t \sum_{\lambda_1}^{\lambda_2} Q(\lambda, t') \Delta\lambda \Delta t'. \quad (17)$$

3.4. Quantum yield of CQ conversion

As camphorquinone is irradiated, it is photoconverted and loses its absorption properties. The loss of absorption by CQ corresponds to conversion of CQ. The concentration $C(t)$ of the remaining CQ (number of CQ molecules/volume) as a function of curing time t is given as:

$$C(t) = \left(\frac{\mu_{\text{ao},\lambda}}{\varepsilon_\lambda \ln 10} \right) \left(\frac{N}{\text{liter}} \right) \exp \left(-\frac{E_{\text{total}} t}{H_{\text{threshold}}} \right), \quad (18)$$

where $\mu_{\text{ao},\lambda}$ is the CQ initial absorption coefficient at wavelength λ , ε_λ the CQ molar extinction coefficient at λ , N the Avogadro's constant, and $H_{\text{threshold}} (=E_{\text{total}} \times \tau)$ again is the radiant exposure threshold (where CQs concentration drops to $1/e$). Since there is no numerical solution for Eq. (17), we obtained the relationship between the CQ concentration and the accumulated number of absorbed photon density by plotting C versus A_{photon} for all time points. The slope of this relationship is the CQ consumption per absorbed photon, that is the quantum yield of CQ conversion.

4. Results

4.1. Molar extinction coefficient of CQ

The absorption coefficient of unirradiated CQ increases proportionally at 469 nm with concentration (Fig. 5). The slope of the regression line is $105 \pm 5 (\text{mol/L})^{-1}$, and since the relationship between μ_a and C is $\mu_a = (\ln 10)\varepsilon_{469}C$, where the molar extinction coefficient $\varepsilon_{469} = 46 \pm 2 \text{ cm}^{-1}/(\text{mol/L})$, the molar extinction coefficient ε_{469} at 469 nm of CQ is $46 \pm 2 \text{ cm}^{-1}/(\text{mol/L})$.

4.2. CQ absorption versus illumination time

Fig. 6 shows the absorption coefficient μ_a as a function of wavelength for resin containing 0.7% CQ for five different illumination times for irradiance $E_{\text{total}} = 160 \text{ mW/cm}^2$ in absorption spectrum method. There is no shift in absorption peak (always at $469 \pm 1 \text{ nm}$) throughout the illumination time. For this curing irradiance, the absorption coefficient μ_a at five dif-

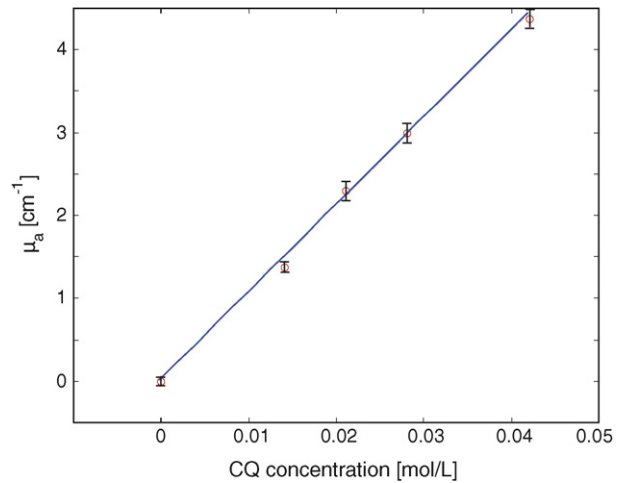


Fig. 5 – The absorption coefficient μ_a at wavelength $469 \pm 1 \text{ nm}$ as a function of CQ molar concentration, C , (mol/L) in resin. The slope of the regression line is $105 \pm 5 (\text{mol/L})^{-1}$. The error bars are the standard deviations of three sample measurements.

ferent wavelengths (410, 430, 450, 470, and 490 nm) as a function of curing time was plotted in Fig. 7 (dots) and fitted with Eq. (13). The result fitting parameters for eight wavelengths are listed in Table 2.

The resin absorption coefficient at 469 nm as a function of illumination time for the LED curing lamp (absorption spectrum method) is plotted in Fig. 8; while Fig. 9 is the result for the QTH curing lamp (transmitted spectrum method). The fitted parameters μ_{ao} and τ are summarized in Table 1. The radiant exposure, $H_{\text{total}} = \tau E_{\text{total}}$ (the product of the irradiance and time of illumination [9]) is the same for all the measurements (ANOVA: $p < 0.05$).

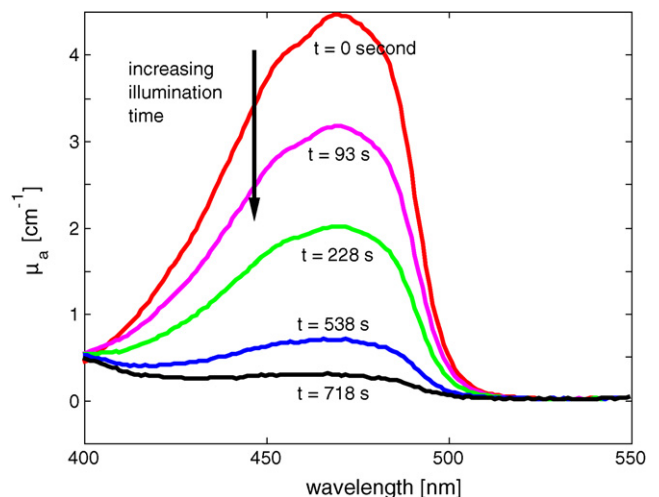


Fig. 6 – The absorption coefficient μ_a as a function of wavelength of resin with 0.7% CQ at five different illumination times for irradiance $E_{\text{total}} = 160 \text{ mW/cm}^2$ (absorption spectrum method). As the time of illumination increases, the absorption decreases.

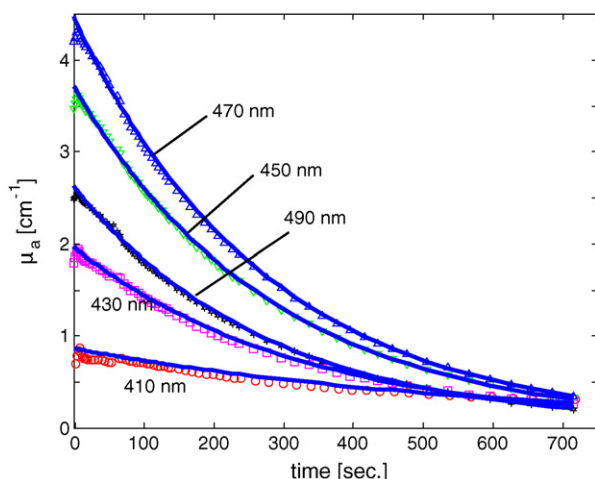


Fig. 7 – The absorption coefficient μ_a at five different wavelengths as a function of curing time for irradiance $E_{\text{total}} = 160 \text{ mW/cm}^2$ (absorption spectrum method). The dots are the data and the lines are the fitted exponential function. The fitted parameters are listed in Table 2.

Table 2 – μ_{a0} and τ are the fitting parameters of the exponential model (Eq. (13)) for eight different wavelengths

Wavelength (nm)	$\mu_{a0} (\text{cm}^{-1}) \pm 0.01$	$\tau (\text{s}) \pm 1\%$
400	0.52	2494
410	0.82	600
430	1.95	326
450	3.70	284
470	4.45	277
490	2.61	276
500	0.55	300
510	0.09	430

4.3. Photon absorption versus illumination time

Fig. 10 depicts the number of absorbed photons per volume per second as a function of wavelength (Eq. (16)) at five different illumination times for an irradiance $E_{\text{total}} = 160 \text{ mW/cm}^2$ (LED lamp). As the time of illumination increases, the number of absorbed photons per second decreases. The accumulated absorbed photons per volume as a function of illumination time (Eq. (17)) is shown in Fig. 11.

The absorption coefficient in Fig. 8 (curve $E = 160 \text{ mW/cm}^2$) was converted to a corresponding CQ concentration (number of molecules per cm^3) using Eq. (18). Then, the CQ concentration was plotted against the accumulated absorbed photon density in Fig. 12 (dots). The regression line describes the quantum yield of CQ conversion, and is 0.066. All other quantum yields for different irradiances are listed in Table 1.

5. Discussion

The molar extinction coefficient of 0.7 wt.% CQ in unfilled BIS-GMA/TEGDMA resin containing an amine and BHT is $46 \pm 2 \text{ cm}^{-1}/(\text{mol/L})$, that is $4.6 \times 10^4 \text{ cm}^2 \text{ mol}^{-1}$. This value is

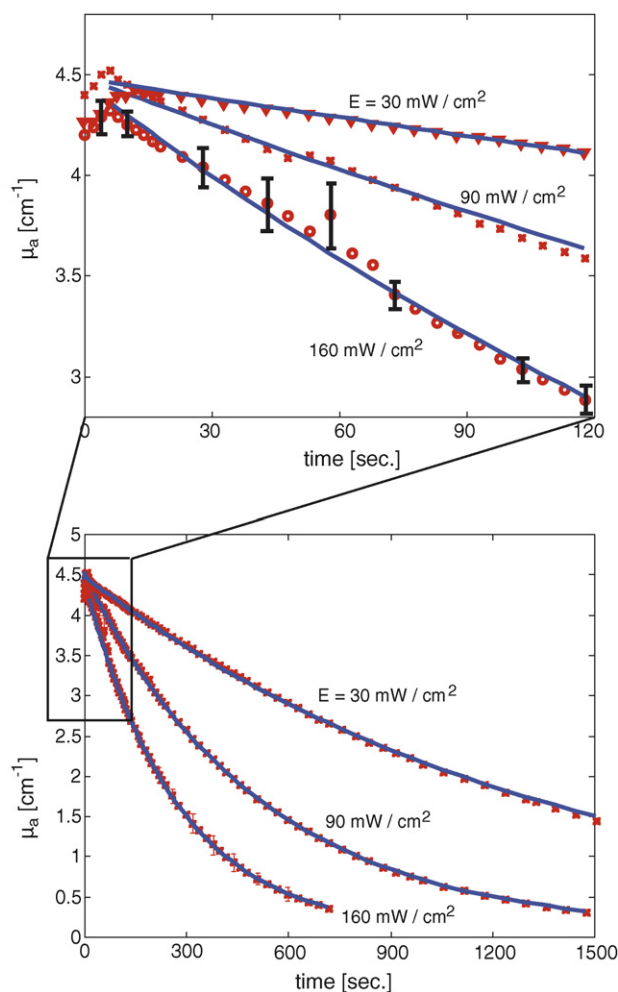


Fig. 8 – Top: the first 120 s data of the resin absorption coefficient μ_{a469} as a function of illumination time for three different irradiances E_{total} (absorption spectrum method). The error bars for 160 mW/cm^2 irradiance are the standard deviations of three sample measurements. Bottom: data from 0 to 1500 s for the three different irradiances. The dots are data measured points and the curves are the fitted exponential function (Table 1).

close to Cook's result, $\sim 3.8 \times 10^4 \text{ cm}^2 \text{ mol}^{-1}$ for 0.25 wt.% CQ in dimethacrylate resins with 0.3 wt.% amine as a coinitiator [2].

The absorption peak (around 469 nm) of CQ decreased as light exposure proceeded until it was close to zero. However, the absorption curve shown in Fig. 6 is pinned on the left side with a positive absorption at 400 nm. Fig. 6 and Table 2 also show that the absorption decay constant was slower at 400 nm ($\tau = 2494 \pm 25 \text{ s}$) than at 470 nm ($\tau = 277 \pm 3 \text{ s}$). Since during the photoreaction, that is the proton abstraction process, the trimethylnorcamphane part of the CQ structure remains unchanged [6], it is likely that the trimethylnorcamphane is responsible for the short-wavelength (UV) absorption at 400 nm. However, further study is needed to verify this. Davidenko et al. studied the efficiency of titanocene photoinitiator in the polymerization of a TEGDMA-based dental material [13]. The absorption of titanocene under irradiation with visible

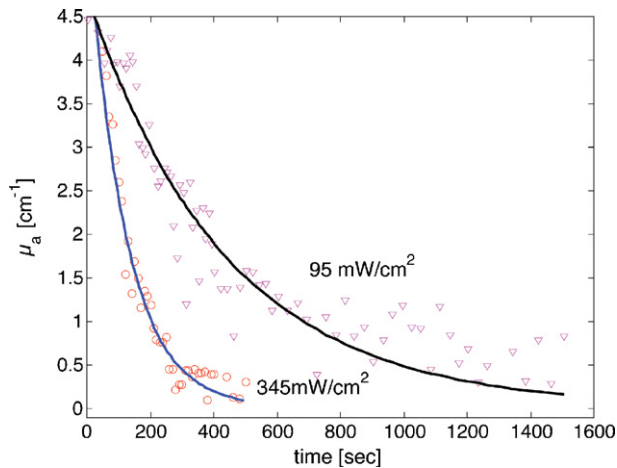


Fig. 9 – The CQ + resin absorption coefficient at 469 nm as a function of illumination time for two different irradiances using the QTH lamp as the light source (transmitted spectrum method). The dots are data and the curves are the fitted exponential function (Table 1).

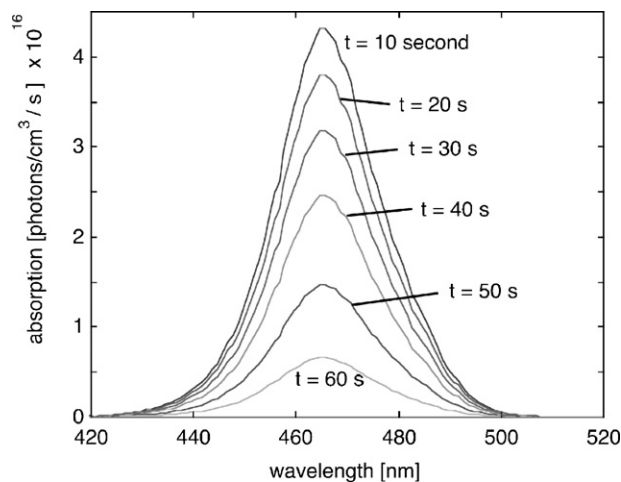


Fig. 10 – The number of photons absorbed by CQ per volume per second as a function of wavelength at five different illumination times for irradiance $E_{\text{total}} = 160 \text{ mW/cm}^2$ in absorption spectrum method.

light decreased around the absorption peaks in the visible range ($>400 \text{ nm}$) but was pinned at $\sim 380 \text{ nm}$, and the absorption even inversely increased with irradiation at wavelengths shorter than 380 nm .

The CQ absorption coefficient increased at the beginning of light illumination. For the low radiant exposure ($<0.1 \mu\text{J/cm}^2$) produced from the Cary spectrophotometer, we saw a gradual increase in absorption over the 60 scans (Fig. 3). For higher irradiances ($\geq 30 \text{ mW/cm}^2$), the absorption of CQ increased by about 0.13 cm^{-1} ($\sim 3\%$ increase) during the first 8 s for all three different irradiances using the LED in absorption spectrum method (Fig. 8). We did not see this increase in transmitted spectrum method, because the fluctuation of the QTH lamp for the second method was more than 5%.

Since the absorption of resin without CQ is nearly zero at 469 nm (0 ± 0.002) (Fig. 5), the only component of the resin system that can change the absorption characteristics at 469 nm must be related to CQ. However, it is not possible at this time to present a likely reason for this change. Several possible explanations can be proposed, but none seem adequate. For example, the increase in absorption might be attributed to specular reflectance changes at the interface between the glass slide and the resin. The index of refraction of the resin increased from 1.50 to 1.53 during curing. If the refractive index of a glass slide is 1.49, then the Fresnel reflectance at the interface will increase from 1×10^{-5} to 3×10^{-4} . For light going through air-glass-resin-glass-air interfaces, the transmission of the light is 92.14% before curing and 92.11% after curing. But for this decrease in transmission, the expected absorption coefficient increase would be less than 0.01 cm^{-1} .

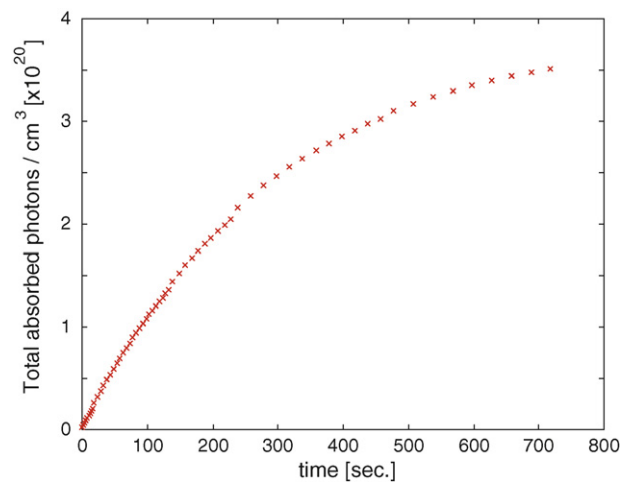


Fig. 11 – The accumulated absorbed photons, $A_{\text{photon}}(t)$, per volume as a function of illumination time for irradiance $E_{\text{total}} = 160 \text{ mW/cm}^2$ in absorption spectrum method.

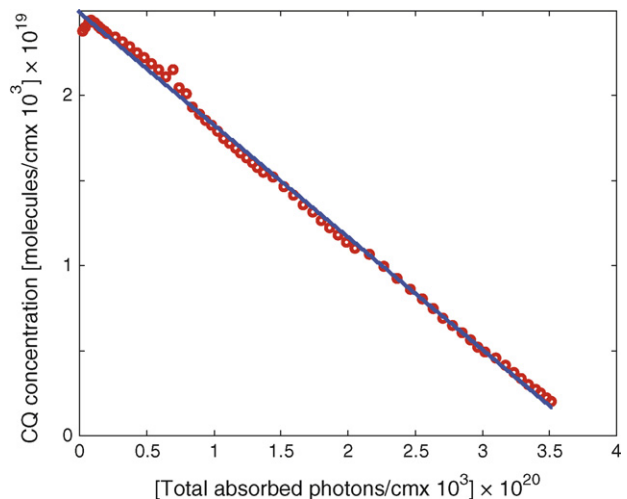


Fig. 12 – CQ concentration as a function of accumulated absorbed photons. The slope of the regression line, the quantum yield of CQ conversion, is equal to 0.0661 ± 0.0002 for irradiance $E_{\text{total}} = 160 \text{ mW/cm}^2$ in absorption spectrum method.

Another possibility is the potential for debonding of resin from the surface of the glass due to the polymerization shrinkage. It was observed that the resins shrank toward the middle illumination spot during the irradiation, but no obvious debonding at the illumination spot could be visually observed. Some interference patterns (color fringes) were observed on the surface of the glass slide at the end of the experiments. However, further investigation is needed to verify whether the fringes were truly produced by a debonding effect.

An other possible explanation for the initial increasing absorption is that a radical intermediate of the CQ may have been formed and increased the absorption. However, we did not find any literature to support this hypothesis, so further study is required.

Beyond the first 8 s of illumination, the absorption of CQ resin decreases exponentially with curing time (Figs. 7–9). The decay time constant τ in Eq. (13) is the same for μ_a at 450–490 nm (ANOVA: $p=0.05$). The time constant decreases as the irradiance increases. Therefore, the product of the irradiance, E_{total} , and the time constant, τ , is a constant, $43 \pm 4 \text{ J/cm}^2$, for all the irradiances using two different curing units and measurement methods (ANOVA: $p=0.05$) (Table 1). This constant represents the curing threshold required for CQ to drop to 1/e of its original concentration. Many other studies have also shown this reciprocity rule [10,12,14–16]. Emami and Soderholm tested the relationship among the degree of conversion, the irradiance, and the radiant exposure (called “light energy per area” in their paper) of two commercially available dental composites (Z100 and Z250) and found that equivalent radiant exposure gave similar conversion values for a certain sample thickness [14].

The exponential decay relationship between the CQ absorption and the radiant exposure in Eq. (14) gives the linearity of the plot of CQ concentration versus total absorbed photon density shown in Fig. 12. That is, this relationship ensures the constant quantum yield of the CQ conversion during curing. On the other hand, the reciprocity rule between the irradiance and the curing time gives the constant quantum yield of the CQ conversion for different irradiances. Our results verify that five different irradiances from two different lamps give essentially the same quantum yield conversion, 0.07 ± 0.01 (ANOVA at $p=0.05$) (Table 1). This means that for this resin formulation, 14 photons must be absorbed to cause one CQ molecule to be photobleached. This finding is similar to that reported by others [3,6]. Nie et al. also found the quantum yield of CQ conversion to be 0.07 ± 0.01 for TEGDMA with CQ as a photoinitiator and *N,N*-DMT as a coinitiator [3]. Monroe and Weiner found that quantum yields for the disappearance of CQ in the same range, being 0.018 ± 0.003 in methanol and 0.057 ± 0.006 in isopropyl alcohol [6].

The efficiency of absorbed photons to convert the photoinitiator depends on many factors. While each absorbed photon definitely creates an excited singlet state, there is the potential for some loss in efficiency in moving from the excited singlet state to the “converted” state. Although intersystem crossing to a triplet excited state is efficient, occurring on the pico second scale, it is still possible for the singlet excited state to return to the ground state (this occurs on a nano second scale). Once, the triplet-state CQ forms, it must then abstract a proton. If this does not happen, it will return to the ground

state. Therefore, one may optimize the proton abstraction by increasing the amine concentration. Once CQ has abstracted a proton, the CQ^*H radical can give a proton back to the solvent or amine, again returning CQ to its ground state. Also two CQ^*H radicals may react to form a CQ^*H_2 alcohol and one CQ molecule in the ground state (this process would lead to two photons required to convert one CQ). Therefore, different photoinitiators and different resin formulations may have different quantum yield values. To further characterize the intermediate semiquinone radicals, electron spin resonance spectrophotometry can be used [6].

By knowing the quantum yield conversion of the photoinitiator in a dental composite, the light dose required to totally convert the photoinitiators can be predicted. However, the relationship between the CQ conversion and the free radical addition polymerization needs further investigation to directly relate the number of absorbed photons to the amount of polymer formed (i.e. the polymerization quantum yield) and the amount of monomer consumed (i.e. the quantum yield of monomer conversion).

6. Conclusions

In general, we have constructed a global principle of how the measurement can be performed and detailed how the quantum yield conversion can be calculated. This method can be applied to any photosensitizer measurement. We have shown that two different light sources, the LED and the 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. We have shown that CQ absorption coefficient decreases exponentially as a function of illumination time. The reciprocity relationship between the irradiance and exposure time holds for changes of CQ absorption coefficient. Further studies are necessary to determine the reason for the initial increase of CQ absorption and to characterize the intermediate products during the curing process.

Acknowledgements

The authors would like to thank Esstech Corp. for supplying the resins. This work was supported by grants from the National Institute of Health, Grant NIH-CI-R24-CA84587-04 and NIH-NIDCR-DE07079.

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