Quantum Yield of Conversion of The Dental Photoinitiator Camphorquinone

Yin-Chu Chen[a], Jack L. Ferracane[b], Scott A. Prahl[a]
[a]Department of Biomedical Engineering, OHSU, Portland, OR
[b]Division of Biomaterials & Biomechanics, OHSU, Portland, OR

ABSTRACT

The primary absorber in dental resins is the photoinitiators, which start the photo polymerization process. We studied the quantum yield of conversion of camphorquinone (CQ), a blue light photoinitiator, using 3M FreeLight LED lamp as the light curing unit. The molar extinction coefficient, ε_{469}, of CQ was measured to be $46\pm2\,\mathrm{cm}^{-1}/(\mathrm{mol/L})$ at 469 nm. The absorption coefficient change to the radiant exposure was measured at three different irradiances. The relationship between the CQ absorption coefficient and curing lamp radiant exposure was the same for different irradiances and fit an exponential function: $\mu_{a469}(H) = \mu_{ao}\exp(-H/H_{\mathrm{threshold}})$, where μ_{ao} is $4.46\pm0.05\,\mathrm{cm}^{-1}$, and $H_{\mathrm{threshold}}$=$43\pm4\,\mathrm{J/cm}^2$. Combining this exponential relationship with CQ molar extinction coefficient and the absorbed photon energy (i.e., the product of the radiant exposure with the absorption coefficient), we plotted CQ concentration [number of molecules/cm^3] as a function of the accumulated absorbed photons per volume. The slope of the relationship is the quantum yield of the CQ conversion. Therefore, in our formulation (0.7 w% CQ with reducing agents 0.35 w% DMAEMA and 0.05 w% BHT) the quantum yield was solved to be 0.07 ± 0.01 CQ conversion per absorbed photon.

Keywords: Photo-cured dental composite, curing efficiency, molar extinction coefficient

1. INTRODUCTION

Photo-cured composites have been widely used in dental restorations.[1] Generally, a composite consists of a mixture of resins with photoinitiators and silane-coated, inorganic filler particles. The photoinitiator absorbs light, and is promoted to an excited state that interacts with a photoreducer (a electron or proton donor molecule) to initiate a free radical addition polymerization of the resin monomers. Camphorquinone (CQ), a blue light photoinitiator, is commonly used in dental resin formulations.[2] CQ is di-2,3-diketo-1,7,7-trimethylnorcamphane with molecular weight of 166.2 and has an absorption peak around 469 nm.

The photo-curing efficiency, defined as extent of cure per delivered photon, has been widely discussed in photo-cured composite systems by evaluating the extent of cure or curing depth for different composite formulations[3–5] or for different light curing units.[6–8] However, these studies were specific to a particular combination of curing units and materials and lacked the information of the actual number of photons absorbed for extent of cure. Some studies[7,8] suggested a "integrated relative curing potential" ($ICPrel$) parameter defined as

$$ICPrel = \int_{\lambda_1}^{\lambda_2} E(\lambda)A(\lambda)d\lambda \ ,$$

where $E(\lambda)$ is the spectral irradiance of the curing unit, $A(\lambda)$ is the relative absorbance of photoinitiator, and λ_1–λ_2 is the wavelength range of the curing unit. In fact, if we substitute above $A(\lambda)$ with the absorption coefficient $\mu_a(\lambda)$ of the photoinitiator, above equation represents the total absorbed energy per unit volume in the material (according to the CIE/ISO definition[9]). This parameter gives the effective photon absorption in the material. However, not all the light absorbed by the materials is equally effective at inducing polymerization. The primary absorption in resins is by the photoinitiator and the absorption drops during the curing process,[10] which, in turn, may decrease the polymerization rate.

Further author information: (Send correspondence to S. A. P.)
Y.-C. C.: E-mail: yinchu@bme.ogi.edu, Tel: (503) 216-6830
S. A. P.: E-mail: prahl@bme.ogi.edu, Tel: (503) 216-2197

Proceedings of SPIE Vol. 5771, p. 256–266, Saratov Fall Meeting 2004: Optical Technologies in Biophysics and Medicine VI; Valery V. Tuchin; Ed.

This research studied the relationship between the changes of photoinitiator absorption and the light radiant exposure. Combining this relationship with CQ's molar extinction coefficient, we were able to quantify the quantum yield Φ of CQ conversion.

$$\Phi = \frac{\text{Number of converted CQ molecules}}{\text{Number of absorbed photons}} \ .$$

2. THEORY

2.1. Irradiance of the curing illumination

The spectral power per nm at wavelength λ of the lamp, $P(\lambda)$, can be represented as

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

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

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

Since the spatial irradiance across the illumination spot has a Gaussian distribution, assume that w is the width of the beam (where the irradiance drops 1/e), and assume $E(\lambda, r)$ is the spectral irradiance at wavelength λ and position r and has a unit of (power)/(area)/(nm), then

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

Therefore, the average irradiance at wavelength λ over the absorbance detection area (assuming the area has a radius r_0) becomes

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

The total irradiance over the r_0 area is

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

2.2. Relationship between CQ's absorption and lamp's illumination time

The absorption coefficient as a function of illumination time was assumed to be an exponential function,[1, 11]

$$\mu_a(\lambda, t) = \mu_{ao}(\lambda) \exp(-t/\tau) \ , \tag{2}$$

where $\mu_{ao}(\lambda)$ and τ are the fitting parameters. Physically, $\mu_{ao}(\lambda)$ is the initial absorption coefficient at wavelength λ at time 0, and the time constant τ depends on the spectral irradiance of curing lamp and CQ's quantum yield.

2.3. Number of photons absorbed by CQ

The number of photons delivered by the lamp per cm^2 per second as a function of wavelength $N_{\text{photon}}(\lambda)$ is

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

where $E(\lambda)$ is the irradiance at wavelength λ, h is Planck's constant, ν is frequency of light, and c is the speed of light.

The number of photons absorbed by CQ per cm^3 per second as a function of wavelength at time t is $N_{\text{photon}}(\lambda)$ minus transmitted photons divided by the thickness of the sample, k.

$$Q(\lambda, t) = \frac{N_{\text{photon}}(\lambda)}{k} (1 - e^{-\mu_a(\lambda, t)k}) \ . \tag{3}$$

Therefore, the accumulated number of photons, $A_{\text{photon}}(t)$, absorbed by CQ per cm^3 at time t is equal to the integration of $Q(\lambda, t)$ over all wavelength and through time t:

$$A_{\text{photon}}(t) = \int_0^t \int_\lambda Q(\lambda, t') d\lambda dt' \ . \tag{4}$$

2.4. Quantum yield of CQ conversion

Assume that once the CQ molecule is converted, the CQ loses its absorption property. Then, from CQ's absorption coefficient as a function of time (Eq. 2) and CQ's molar extinction coefficient (ε_λ) at wavelength λ, we can calculate CQ's concentration, $C(t)$, with unit of [number of CQ molecules/cm^3] as a function of curing lamp illumination time t:

$$C(t) = \left(\frac{\mu_{a\lambda}}{\varepsilon_\lambda \ln 10}\right)\left(\frac{N}{\text{liter}}\right)\exp(-t/\tau) \ , \tag{5}$$

where N is Avagado's constant and liter is 1000 cm^3/L. By comparing Eq. 4 and Eq. 5, at the same time point t, the relationship of the concentration of CQ versus the accumulated number of absorbed photon density ($C(t)$ versus $A_{\text{photon}}(t)$) can be obtained. The slope of this relationship is the CQ consumption per absorbed photon, that is the quantum yield of CQ conversion.

3. MATERIALS AND METHODS

3.1. Materials

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

3.2. CQ absorption versus CQ concentration

To measure the absorption coefficient as a function of CQ concentration, resin solutions with 5 different CQ concentrations (0, 0.26, 0.35, 0.52, and 0.7 w%) were filled into 4 mm cuvettes and sealed 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 to 400 nm. This spectrophotometer is a dual channel system: one channel is for the sample and the other is for a reference sample. A 4 mm cuvette filled with water was used as the reference sample for these measurements.

3.3. CQ absorption versus radiant exposure

We used Cary spectrophotometer to measure the absorption coefficient of resin with 0.7% CQ as a function of illumination time for three different irradiances. A 3M FreeLight LED lamp (3M ESPE, Seefeld, Germany) with a 7 mm diameter illumination tip was chosen as the light curing unit, whose illumination peak at 465 nm with narrow bandwidth (FWHM = 24 nm) is close to CQ's absorption peak at 469 nm. 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 FreeLight was placed at three different distances, 10, 15, and 27 mm, away from the surface of the sample. The FreeLight was fully charged before each irradiance measurement.

The experimental setup inside the Cary spectrophotometer chamber is shown in Fig. 1. To reduce the effects of non-uniform light dose through the sample (the front illumination receives more light than the back), 1 mm thick glass-slide cuvettes (bottom and side sealed with Epoxy glue) were made to contain the resin. Consequently, 0.7 w% CQ resin corresponds to an optical thickness of less than 0.45; in other words, the difference between front and back is always less than 36%. The sample arm was resin with 0.7% CQ (called "CQ resin"). The reference arm was resin without CQ.

To minimize the effects of non-uniform irradiance (which was Gaussian) across the FreeLight illumination area, we blocked half of the spectrophotometer beams (width by height = 1×10 mm) of both channels such that a rectangular 1×5 mm of beam was sent to the samples. According to our irradiance measurement, the FreeLight irradiance deviation across that 5 mm height was less than 15% (for FreeLight positioned 10 mm away from the sample). This also had the advantage of reducing the irradiating energy from the spectrophotometer beam. The power of the spectrophotometer beam was lower than the detection limit, 0.1 μW, of the power meter (LiCONiX

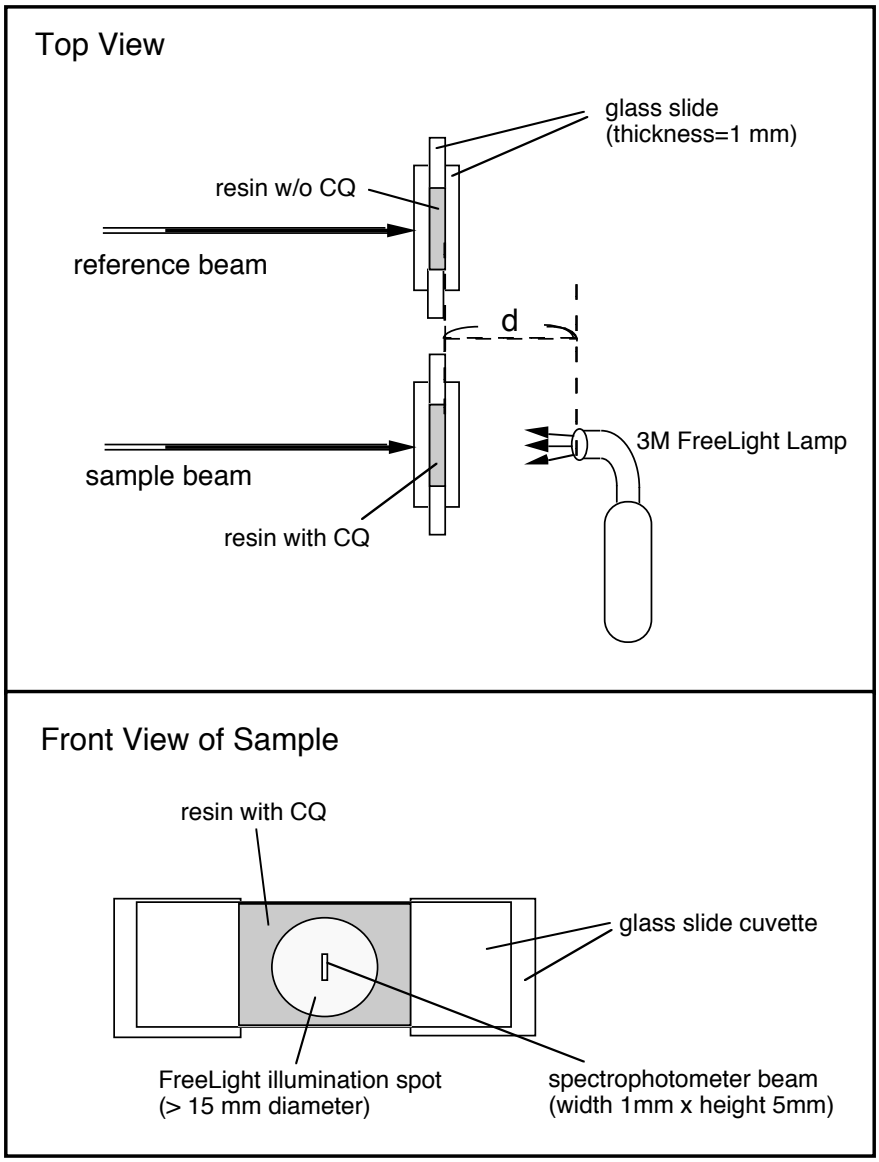

Figure 1. Experimental setup for dynamic absorption measurements. Top picture is a top view of the chamber of the dual-channel spectrophotometer. Resin without CQ was placed at the reference arm and resin with CQ was in the sample arm. The samples were filled in glass-slide cuvettes with a thickness of 1 mm. The FreeLight lamp 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 FreeLight illumination spot.

45PM Power Meter, Nolatek, Houma, LA). Therefore the radiant exposure for each scan was $<0.1\,\mu J/cm^2/nm$ $(=(0.1\,\mu W) \div (\text{beam area } 1\times 0.1\,cm^2) \times (\text{integration time } 0.1\,s/nm))$.

The illumination position of the FreeLight was adjusted such that the spectrophotometer detecting beam was situated in the center of the illumination spot (see Fig. 1). During the experiment, the positions of both glass-cuvette samples (the sample arm and reference arm) were fixed, thus the spectrophotometer always detected the same spot of the samples. The FreeLight 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 with integration time 0.1 s/nm. The absorbance of the CQ resin was scanned before any illumination started. After this, the experiment was repeated with FreeLight illumination followed by a single absorbance 15 second scan until changes in absorbance were negligible or until the FreeLight maximum functioning time was reached ($\sim$ 30 minutes). The duration of FreeLight illumination started with every 2 seconds followed by an absorbance scan for the first 20 seconds, every 5 seconds for the next 120 seconds, every 10 seconds for the next 100 seconds, every 20 seconds for the next 160 seconds, every 30 seconds for the next 240 seconds, and every 40 seconds for the rest of the time.

The measured absorbance $A(\lambda)$ at wavelength λ was calculated by averaging the absorbance from $\lambda - 1$ to $\lambda + 1$ nm. The absorption coefficient at wavelength λ is $\mu_a(\lambda) = A(\lambda)(\ln 10)/k$, where $k = 0.1$ cm is the thickness of the sample.

3.4. Irradiance distribution over the illumination spot

For the same relative position between the sample and the FreeLight (10, 15, or 27 mm distance for the three irradiances), the spatial distribution of the irradiance of the illumination spot was measured by placing an optical fiber at different positions across the illumination spot (controlled by a micrometer) and detected with the spectrometer. A proper ND filter was used to attenuate the light if the signals were saturated.

4. RESULTS AND DISCUSSION

4.1. Molar extinction coefficient of CQ

The absorption coefficient at 469 nm increases proportionally with CQ concentration (Fig. 2). The slope of the regression line is $105\pm5\,(mol/L)^{-1}$, and so the molar extinction coefficient ε_{469} at 469 nm of CQ is $46\pm2\,cm^{-1}/(mol/L)$.

4.2. CQ absorption versus illumination time

Generally, as the time of illumination increases, the absorption of CQ resin decreases (Fig. 3). There is no shift in absorption peak (always at 469±1 nm) throughout the illumination time. Overall, the relationship between the absorption coefficient and illumination time fit an exponential function within 5% errors (Fig. 4). The result fitting parameters are listed in Table 1. Note that we did not include the first three data points when fitting Eq. 2.

Surprisingly the absorption coefficient increased about $0.13\,cm^{-1}$ during the first 8 seconds for all the irradiances (Fig. 4). Since the absorption at 469 nm of resin without CQ is about zero (Fig. 2), the only component

	w (cm)	E_{total} (mW/cm^2)	μ_{ao} (cm^{-1})	τ (sec)	τE_{total} (mJ/cm^2)	$\tau\sqrt{E_{\text{total}}}$ —	Φ —
	±0.05	±10%	±0.01	±1%	±11%		±0.002
FreeLight#1	0.5	160	4.41	280	44800	3540	0.066
FreeLight#2	0.7	90	4.51	525	47250	4980	0.065
FreeLight#3	1.2	30	4.46	1385	41550	7586	0.068

Table 1. w is the width of the FreeLight illumination spot in Eq. 1. The corresponding irradiance E_{total} is calculated from Eq. 1 for r_0 =0.25 cm. μ_{ao} and τ are the fitting parameters of the exponential model (Eq. 2) for three different irradiances (E_{total}). The standard errors are the fitting errors for the parameters.

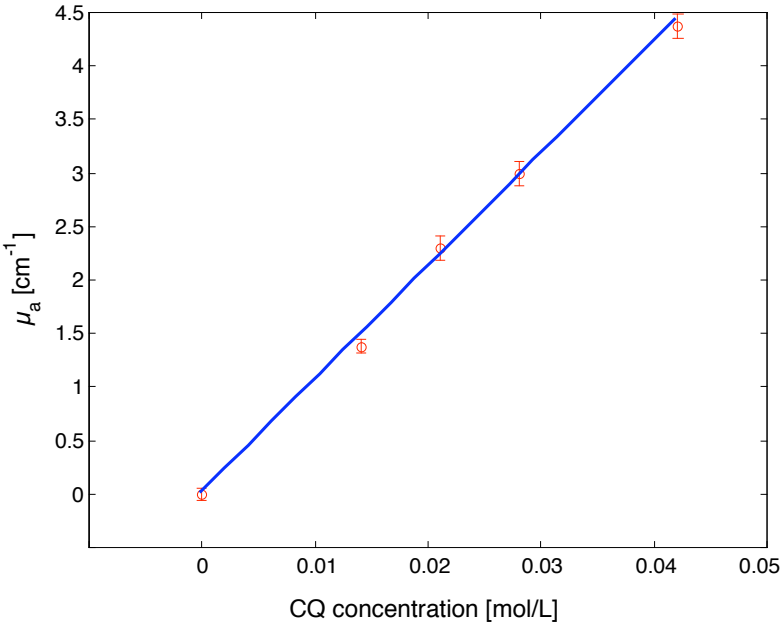

Figure 2. The absorption coefficient μ_a at wavelength 469±1 nm as a function of CQ molar concentration, C, (mol/L) in resin. The relationship between μ_a and C is $\mu_a = (\ln 10)\varepsilon_{469}C$, where the molar extinction coefficient ε_{469}= 46±2 cm^{-1}/(mol/L). The error bars are the standard deviations of three sample measurements.

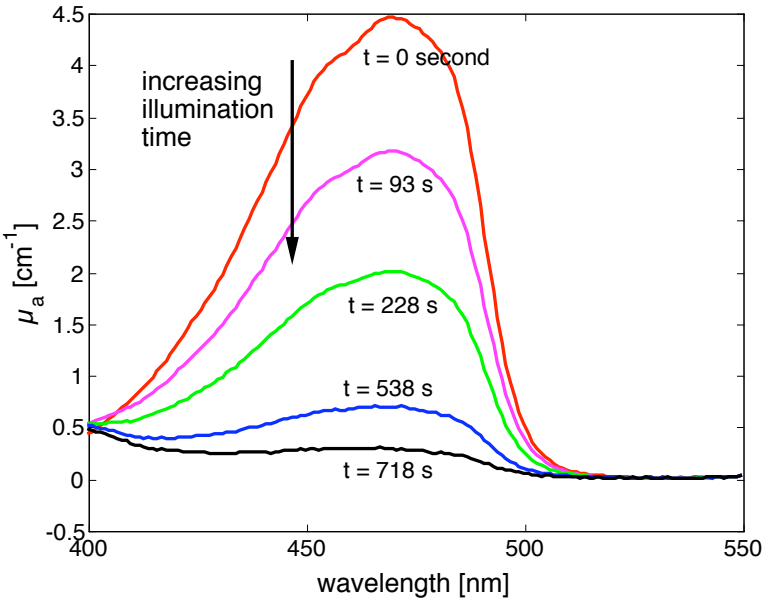

Figure 3. The absorption coefficient μ_a as a function of wavelength of resin with 0.7% CQ at five different illumination times for irradiance E_{total}=160 mW/cm^2. As the time of illumination increases, the absorption decreases.

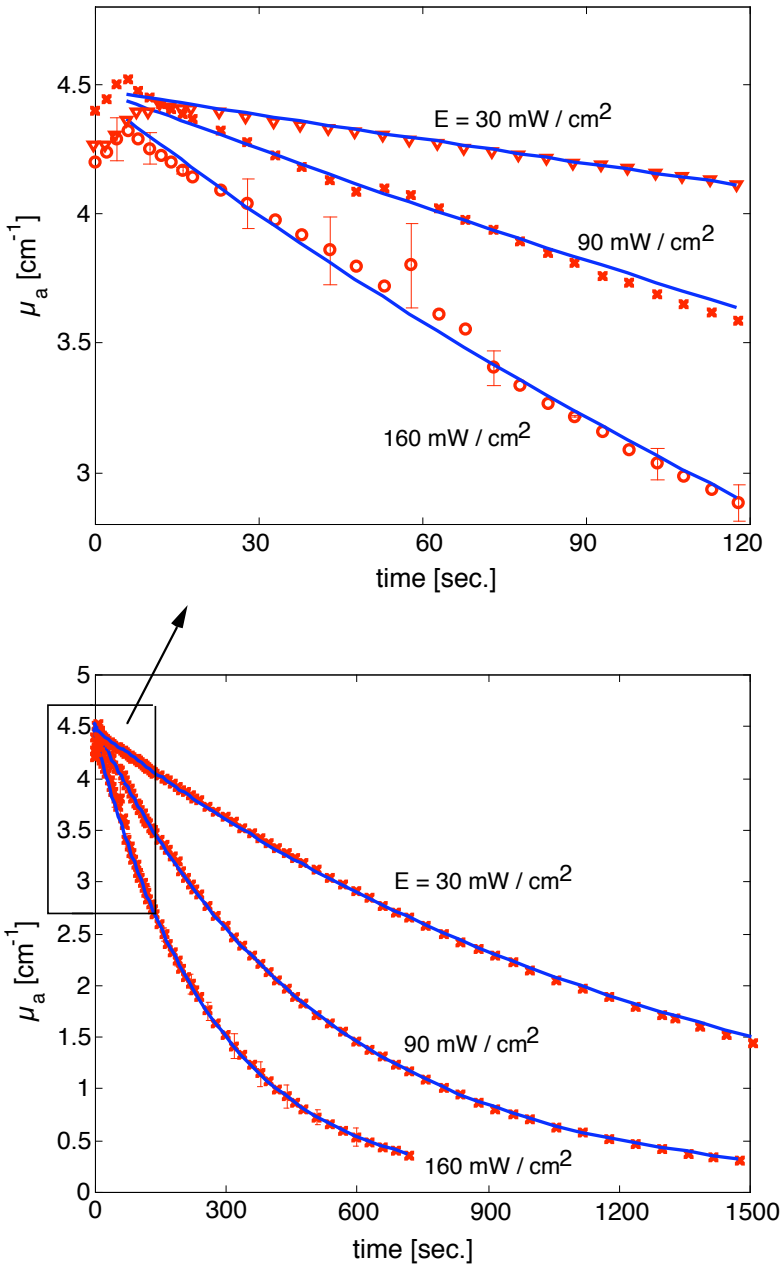

Figure 4. (Top) The first 120 second data of the resin absorption coefficient μ_{a469} as a function of illumination time for three different irradiances E_{total}. The error bars for 160 mW/cm^2 irradiance are the standard deviations of three sample measurements. (Bottom) Data from 0 to 1500 seconds for the three different irradiances. The dots are data and the curves are the fitted exponential function. The fitting parameters are listed in Table 1.

that can change the absorption at 469 nm is CQ. This change in absorption is larger than the increase reflectance at the interface between the glass slide and the resin. The index of refraction of the resin changed from 1.50 to 1.53 during curing. If the refractive index of glass slide is 1.49, then the Fresnel reflectance at the interface will increase from 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. For this decrease in transmission, the expected absorption coefficient increase is less than $0.01\,\mathrm{cm}^{-1}$. One possible explanation is the formation of a combined photosensitizer/reducing agent complex, but further investigation is needed to support this hypothesis.

In Table 1, the product of the irradiance and time of illumination are the same for the three irradianes ($p < 0.05$). This reciprocity between E_{469} and t is consistent with some previous findings.[4, 10–13] Since the product of irradiance and time is radiant exposure, H, the result gives

$$\mu_{a469}(H) = \mu_{ao}\exp(-\frac{H}{H_{\mathrm{threshold}}}) \ , \tag{6}$$

where μ_{ao} is $4.46\pm0.05\,\mathrm{cm}^{-1}$ at 469 nm, and $H_{\mathrm{threshold}} = \tau E_{\mathrm{total}}$=$43\pm4\,\mathrm{J/cm}^2$.

4.3. Photon absorption versus illumination time

Figure 5 depicts the spectrum of the number of absorbed photons per cm^3 per second as a function of wavelength (Eq. 3) at five different illumination times for irradiance E_{total}=$160\,\mathrm{mW/cm}^2$. As the time of illumination increases, the unit time of photon absorption decreases. For the same irradiance, the accumulated absorbed photons per cm^3 as a function of illumination time (Eq. 4) is shown in Fig. 6.

The absorption coefficient in Fig. 4 (curve E=$160\,\mathrm{mW/cm}^2$) can be converted to corresponding CQ concentration [number of molecules per cm^3] using Eq. 5. Then, the CQ concentration was plotted against the accumulated absorbed photon density in Fig. 7 (dots). The regression line of the dots, the quantum yield of CQ conversion, is 0.0661 ± 0.0002. All other quantum yields for different irradiances are listed in Table 1.

For a single wavelength illumination, which means H is not wavelength dependent and H_{total} becomes the threshold for that single wavelength illumination ($\equiv H_{\mathrm{threshold}}$), we can take the derivative of μ_a to H in Eq. 6.

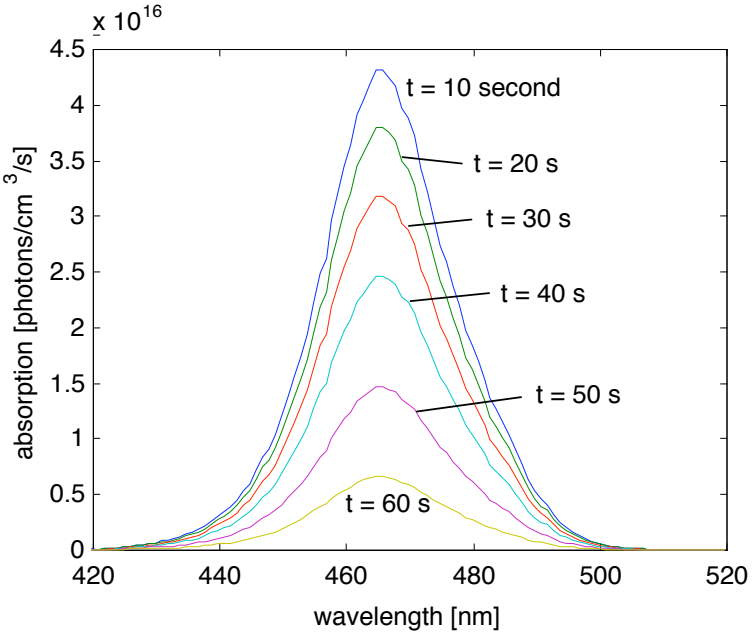

Figure 5. The number of photons absorbed by CQ per cm^3 per second as a function of wavelength at five different illumination times for irradiance E_{total}=$160\,\mathrm{mW/cm}^2$.

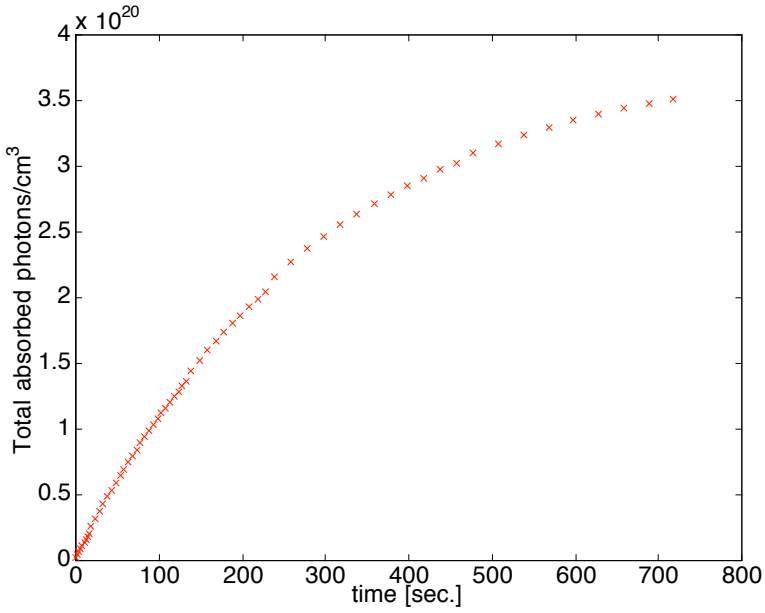

Figure 6. The accumulated absorbed photons, $A(t)$, per cm^3 as a function of illumination time for irradiance E_{total}=160 $\mathrm{mW/cm}^2$.

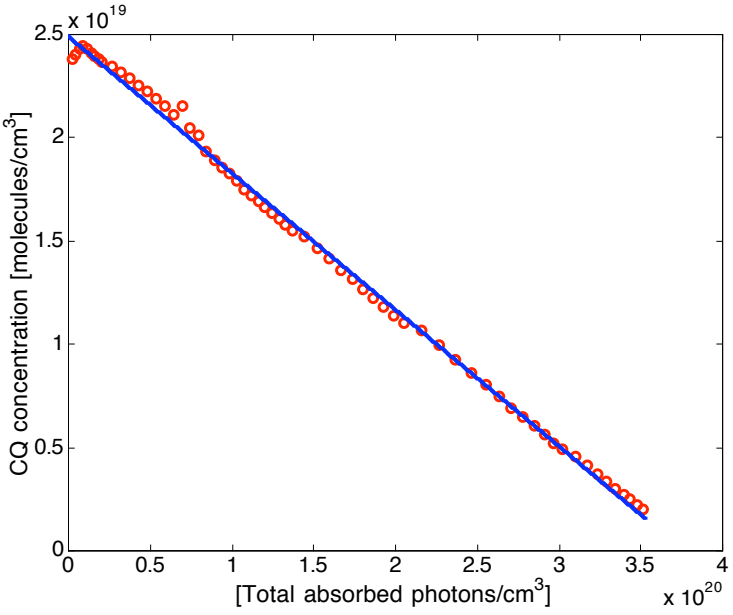

Figure 7. The dots are the data of CQ concentrations (number of molecules per cm^3) as a function of accumulated absorbed photons, $A(t_o)$, per cm^3 for irradiance E_{total}=160 $\mathrm{mW/cm}^2$. The slope of the regression line, the quantum yield of CQ conversion, is equal to 0.0661±0.0002.

Then the equation becomes

$$\Delta\mu_a = -\frac{\mu_{ao}\exp(-H/H_{\text{threshold}})\Delta H}{H_{\text{threshold}}} = -\frac{\mu_a(H)\Delta H}{H_{\text{threshold}}} \quad .$$

The term $\mu_a(H)\Delta H$ is the effective energy density [J/cm^3] absorbed by CQ.

If we combine above equation with Eq. 5 for CQ consumption [number of CQ molecules/cm^3] and convert [J/cm^3] to absorbed photon density, Q [number of photons/cm^3], we can obtain the quantum yield equation:

$$\Phi = \frac{dC}{dQ} = \frac{N}{\text{liter}} \cdot \frac{h\nu}{\varepsilon(\ln 10)H_{\text{threshold}}} \quad . \tag{7}$$

If we substitute $H_{\text{threshold}}$=43±4 J/cm^2 and assume FreeLight spectrum peak 465 nm represents the single wavelength illumination, we can estimate the quantum yield equals to 0.056±0.005. This estimation is about 20% lower than the quantum yield calculated in Table 1, however, not significantly different (ANOVA at $p = 0.05$).

The average quantum yield is 0.07±0.01 for all the measurements, that is about every 14 photon absorption converts 1 CQ. This may be due to reabsorption of CQ when excited CQ goes back to its ground state. Note that a different ratio of reducing agents may have a different quantum yield.

In conclusion, we showed a reciprocity relationship between the irradiance and exposure time for changes of CQ absorption coefficient. Combining this relationship with CQ molar extinction coefficient, one can solve for the quantum yield for the photoinitiator.

ACKNOWLEDGMENTS

The authors would like to thank Dr. Ronald Sakaguchi at Department of Restorative Dentistry, OHSU for use of his resins. This work was supported by the grants from National Institute of Health, Grant NIH-CI-R24-CA84587-04 and NIH-NIDCR-DE07079.

REFERENCES

1. D. C. Watts, *Dental Restorative Materials. In: Materials Science and Technology: A Comprehensive Treatment, Medical and Dental Materials (D. F. Williams, editor)*, VCH Verlagsgesellschaft GmbH, Weinheim, 1992.
2. Q. Yu, S. Nauman, J. P. Santerre, and S. Zhu, "UV photopolymerization behavior of dimethacrylate oligomers with camphorquinone/amine initiator system," *J. Appl. Polym. Sci.* **82**, pp. 1107–1117, 2001.
3. Z. Kucybala, M. Pietrzak, J. Paczkowski, L. A. Linden, and J. F. Rabek, "Kinetic studies of a new photoinitiator hybrid system based on camphorquinone-n-phenylglicyne derivatives for laser polymerization of dental restorative and stereolithographic (3d) formulations," *Polymer* **37**, pp. 4585–4591, 1996.
4. M. Miyazaki, Y. Oshida, B. K. Moore, and H. Onose, "Effect of light exposure on fracture toughness and flexural strength of light-cured composites," *Dent. Mater.* **12**, pp. 328–332, 1996.
5. A. Uhl, R. W. Mills, and K. D. Jandt, "Photoinitiator dependent composite depth of cure and Knoop hardness with halogen and LED light curing units," *Biomaterials* **24**, pp. 1787–1795, 2003.
6. K. D. Jandt, R. W. Mills, G. B. Blackwell, and S. H. Ashworth, "Depth of cure and compressive strength of dental composites cured with blue light emitting diodes (LEDs)," *Dent. Mater.* **16**, pp. 41–47, 2000.
7. F. Stahl, S. H. Ashworth, and R. W. Mills, "Light-emitting diode (LED) polymerization of dental composites:flexural properties and polymerization potential," *Biomaterials* **21**, pp. 1379–1385, 2000.
8. W. Teshima, Y. Nomura, N. Tanaka, H. Urabe, M. Okazaki, and Y. Nahara, "ESR study of camphorquinone/amine photoinitiator systems using blue light-emitting diodes," *Biomaterials* **24**, pp. 2097–2103, 2003.
9. D. H. Sliney and M. L. Wolbarsht, *Safety With Lasers and Other Optical Sources: A Comprehensive Handbook*, Plenum Press, New Yor, 1980.
10. Y. C. Chen, F. L. Ferracane, and S. A. Prahl, "A photon migration model for predicting depth of cure in dental composite," *Dent. Mater.* , submitted.

11. R. H. Halvorson, R. L. Erickson, and C. L. Davidson, "Energy dependent polymerization of resin-based composite," *Dent. Mater.* **18**, pp. 463–469, 2002.
12. N. Emami and K. M. Söderholm, "How light irradiance and curing time affect monomer conversion in light-cured resin composites," *Eur. J. Oral Sci.* **111**, pp. 536–542, 2003.
13. L. Musanje and B. W. Darvell, "Polymerization of resin composite restorative materials: exposure reciprocity," *Dent. Mater.* **19**, pp. 531–541, 2003.