

## Absorbance Spectra Analysis of Photosensitizer and Reducing Agent for Dental Light-cured Resin Monomers

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### ABSTRACT

Infrared analysis showed absorbance spectra of photosensitizer (camphorquinone; CQ) or/and reducing agents (dimethylaminoethyl methacrylate; DMAEMA, dimethyl-para-toluidine; DMPT, and diethylaminoethyl methacrylate; DEAEMA) dissolved in bis-GMA, TEGDMA, UDMA and bis-GMA/TEGDMA binary monomer in the wavelength range 300 to 650 nm to examine the spectral characteristics. Total amount (1.0 wt%) of photosensitizer and reducing agent was dissolved in their monomers. They were analyzed immediately after mixing it, or after keeping it for 7 days at 37°C, showing that their absorbance peak ranges were from 450 to 500 nm (about 470 nm) similar to relative intensity peak obtained by visible light curing source. The result suggests that the absorbance peak ranges of photoinitiators (photosensitizer and reducing agent) to resin matrix agree with absorbance peak range of visible light curing source.

### INTRODUCTION

The photosensitizer (camphorquinone) with reducing agents is used for dental visible light-cured (VLC) composite resins, because the degree of conversion by the

photopolymerization is activated by the components and the content of photoinitiators which are composed of photosensitizer and reducing agent<sup>1-7</sup>. The radiation energy in the wavelength range of 400 to 600 nm was effective to photopolymerize VLC resins when irradiated by visible light to transfer to the excited state<sup>8-10</sup>. In commercial dental composite resins<sup>11</sup> and experimental unfilled VLC resins, the photoinitiators used were analyzed<sup>12-14</sup>. The absorbance behaviour of photosensitizer was analyzed by IR (infrared absorbance) method to form free radicals by visible light irradiation in the wavelength range. The visible light (VL) curing source had the peak ranges of 450 to 470 nm in visible light range<sup>6-10</sup>. The results showed that their wavelength ranges were useful for VL cured resin matrix. This study was thus to evaluate the photosensitizer and reducing agents dissolved in resin monomer and binary monomer mixture in the wavelength range 350 to 600 nm.

### MATERIALS AND METHODS

Polyfunctional methacrylate monomers (triethylene glycol dimethacrylate (TEGDMA; Tokyo Kasei Co, Tokyo), bisphenol-A glycidyl dimethacrylate (bis-GMA, Shin-Nakamura Chem, Wakayama)), UDMA (urethane dimethacrylate, Shin-Nakamura Chem) were tested. 60 wt% bis-GMA/40 wt% TEGDMA binary monomer was mixed in our laboratory, similar to our previous reports<sup>6,7</sup>. The amount of photoinitiators (camphorquinone and reducing agent) was 0.1 to 5.0 wt% to the resin matrix<sup>4,14,15</sup>, and thus the resin monomer and binary monomer mixtures in this study included 1.0 wt% as a total amount to them. The photoinitiators tested were camphorquinone (CQ, Tokyo Kasei Co) as a photosensitizer and reducing agents (DMAEMA; dimethylaminoethyl methacrylate, DMPT; dimethyl-para-toluidine, and DEAEMA; diethylaminoethyl methacrylate,

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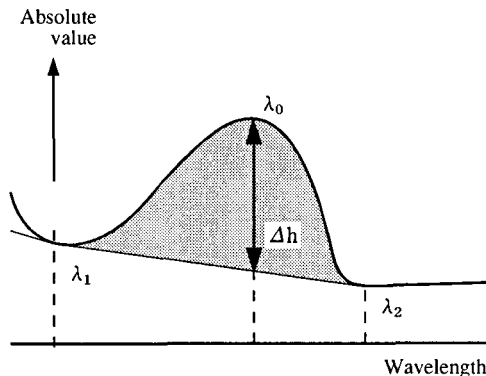
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Tokyo Kasei Co). The absorbance of the photosensitizer (CQ) and photoinitiators (CQ and DMAEMA, CQ and DMPT, CQ and DEAEMA) was measured by the infrared (IR) analysis as follows: Data mode=absolute value, band width=2 nm, time constant=0.4 sec, wavelength set=200 to 600 nm, wavelength scale=20 nm/sec, scan speed=400 nm/min, cell=quartz glass (Nihon Bunkou Kougyou, Tokyo).

## RESULTS

The values measured were three different wavelengths and delta height (delta h) and the area between ramda 1 and ramda 2 (Figure 1). Table 1 indicates absorbance spectra value of bis-GMA, TEGDMA and bis-GMA/TEGDMA when CQ (1.0 wt%) was dissolved, representing that peak value (ramda 0) was approximately 467 nm. The monomer dissolved was obtained immediately after mixing of CQ to resin monomer. Table 2 indicates absorbance wavelengths after keeping it at 37°C for 7 days, showing that the value was 467 nm. Table 3 indi-



**Figure 1** An example of schematic figure; IR chromatogram in the wavelength range. See text for key.

cates absorbance spectra of UDMA to which CQ, CQ and DMAEMA and CQ and DMPT were dissolved (the mixture was kept for 7 days at 37°C). The peak value of wavelength was also approximately 467 nm. Table 4 indicates absorbance spectra of bis-GMA (60)/

**Table 1** Wavelength of absorbance spectra of CQ when dissolved in bis-GMA, TEGDMA and bis-GMA/TEGDMA binary monomer. CQ=1.0 wt%. The mixture was used immediately after mixing of CQ to the resin matrix.

Solvent	CQ (wt%)	Wavelength (nm)			$\Delta h$	Area
		$\lambda_1$	$\lambda_2$	$\lambda_0$		
bis-GMA	1.0	387.0 (2.2)	515.7 (2.6)	466.3 (0.2)	0.152 (0.008)	9.08 (0.54)
TEGDMA	1.0	381.3 (9.6)	520.7 (3.8)	467.9 (0.2)	0.137 (0.002)	8.28 (0.27)
bis-GMA/ TEGDMA	1.0	375.7 (6.9)	513.3 (1.9)	467.5 (0.5)	0.099 (0.043)	5.90 (2.96)

bis-GMA/TEGDMA=60/40

After mixing of CQ to resin matrix (immediately)

**Table 2** Absorbance spectra similarly to Table 1. The mixture was kept for 7 days at 37°C after mixing.

Solvent	CQ (wt%)	Wavelength (nm)			$\Delta h$	Area
		$\lambda_1$	$\lambda_2$	$\lambda_0$		
bis-GMA	1.0	385.3 (2.5)	522.0 (3.3)	466.4 (0.6)	0.197 (0.024)	11.93 (1.52)
TEGDMA	1.0	386.3 (4.2)	518.7 (8.4)	467.7 (0.5)	0.123 (0.015)	7.85 (0.15)
bis-GMA/ TEGDMA	1.0	371.3 (3.4)	517.0 (3.7)	467.9 (0.4)	0.151 (0.024)	9.54 (1.31)

bis-GMA/TEGDMA=60/40

At 37°C (7 days)

**Table 3** Absorbance spectra of UDMA including CQ, CQ and DMAEMA, and CQ and DMPT. See text for key.

Photoinitiators	Wavelength (nm)			$\Delta h$	Area
	$\lambda_1$	$\lambda_2$	$\lambda_0$		
CQ	388.0 (1.6)	515.3 (1.9)	467.1 (0.7)	0.123 (0.001)	7.53 (0.24)
CQ+DMAEMA	385.3 (3.8)	513.3 (1.9)	467.6 (0.0)	0.133 (0.004)	7.89 (0.47)
CQ+DMPT	390.7 (3.4)	516.7 (0.9)	467.7 (0.9)	0.125 (0.005)	7.27 (0.50)

Monomer; UDMA  
At 37°C (7 days)

**Table 4** Absorbance spectra of CQ and DMAEMA, CQ and DMPT, and CQ and DEAEMA in bis-GMA (60)/TEGDMA (40) binary monomer mixture.

Photoinitiators	Wavelength (nm)			$\Delta h$	Area
	$\lambda_1$	$\lambda_2$	$\lambda_0$		
CQ+DMAEMA	379.3 (9.0)	522.0 (2.8)	467.6 (0.0)	0.152 (0.006)	9.00 (0.35)
CQ+DMPT	389.3 (2.5)	518.0 (1.6)	467.7 (0.4)	0.138 (0.005)	8.10 (0.16)
CQ+DEAEMA	386.0 (2.8)	518.7 (4.1)	467.7 (0.4)	0.151 (0.006)	9.01 (0.62)

Comonomer; bis-GMA/TEGDMA=60/40  
Photosensitizer + reducing agent; 1.0 wt% (total)  
At 37°C (7 days)

TEGDMA (40) binary monomer mixture to which CQ and DMAEMA, CQ and DMPT and CQ and DEAEMA were dissolved (kept for 7 days at 37°C), and the peak value was approximately 467 nm.

## DISCUSSION

The wavelength peak range needed for photopolymerization of VLC composite resins was supposed to be approximately 470 nm as shown during direct irradiation of VL curing, showing that the wavelength peak of visible light source was 450 to 500 nm for VLC composite resins<sup>8,10-13</sup>. Greater integrated spectral irradiance (470 to 480 nm) improved curing performance of dental bis-GMA/TEGDMA based unfilled resins<sup>12</sup>.

The photopolymerization varied with the concentrations of photoinitiators (photosensitizer and reducing agent)<sup>12,14</sup>. At CQ=0.5% and more than 0.5 wt%, the degree of photopolymerization was 76% in UDMA/TEGDMA-based unfilled resins containing CQ and

DMAEMA<sup>14</sup>. The formation of free radicals occurred when irradiated by visible light, and reducing agents in VLC resins were used with CQ. The absorption of one quantum of radiation promoted the carbonyl groups to an excited state and returned to the ground state by fluorescence. The content of CQ and inhibitor controlled the magnitude of conversion (photopolymerization) in the monomer mixtures<sup>11</sup>. The varying concentration of CQ and DMAEMA exhibited different value of the degree of conversion in UDMA/TEGDMA based resins<sup>14</sup>. CQ content in the set resins analyzed similarly to those reported by FT-IR (Fourier transform-infrared spectroscopy) and GC methods<sup>12</sup>. Cook reported that the ineffective wavelength occurred at less than 410 nm and greater than 500 nm for CQ<sup>9</sup>. These results suggest, as reported by Hirose et al<sup>12</sup>, that the wavelength range must be selectively filtered. In the wavelength around 705 nm with a strong spectral emission, this radiation was not effective in the photopolymerization. As described

already in this study, the number of quanta spectrum of radiation absorbed by CQ was the integral of the product of the absorption by the spectral intensity of VL curing source.

This study clarified that CQ absorbed with a peak (470 to 480 nm) between 400 to 500 nm and the other photosensitizers absorbed below 400 nm range. The photosensitizer as acceptor accelerated resin monomers with reducing agents and forms free radicals in VLC resins. The compositions in resin composites were chosen out of consideration of viscosity and suitable ratio between reactive groups. Thus, the additions of photosensitizer and reducing agent were important with VL curing of VLC resins. CQ was effective as a photosensitizer system with an absorbance peak (around 470 nm) during VL curing.

### SUMMARY

The photosensitizer (CQ) or/ and reducing agents (DMAEMA, DMPT and DEAEMA) showed absorbance spectra in the wavelength range of 375 to 520 nm and a peak at 467 nm when dissolved in bis-GMA, TEGDMA, UDMA and bis-GMA/TEGDMA. The addition of CQ, or CQ and reducing agents to bis-GMA, TEGDMA and bis-GMA/TEGDMA was effectively available as shown by Infrared method of absorbance spectra, because the spectral peak range agreed with that of VL curing source. The result suggests that additive photoinitiators are used for visible light-cured resins as bis-GMA/TEGDMA resin matrix.

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### REFERENCES

- 1) Asmussen, E.: NMR-analysis of monomers in restorative resins. *Acta Odontol. Scand.* 33, 129-134, 1975.
- 2) Antonucci, J.M., Grams, C.L. and Termini, D.J.: New initiation systems for dental resin based on ascorbic acid. *J. Dent Res.* 58, 1887-1899, 1979.
- 3) Dulik, D., Bernier, R. and Brauer, G.M.: Effect of diluent monomer on the physical properties of bis-GMA-based composites. *J. Dent. Res.* 60, 983-989, 1981.
- 4) Craig, R.G.: Chemistry, composition and properties of composite resins: Symposium on composite resins in dentistry. *Dent. Clinics N. Am.* 25, 219-239, 1981.
- 5) Shintani, H., Inoue, T. and Yamaki, M.: Analysis of camphorquinone in visible light-cured composite resin. *Dent. Mater.* 1, 124-126, 1985.
- 6) Hirose, T., Wakasa, K. and Yamaki, M.: A visible-light activating unit with experimental light-conductors-photopolymerization in bis-GMA unfilled resins for dental application. *J. Mater. Sci.* 25, 932-935, 1990.
- 7) Urabe, H., Wakasa, K. and Yamaki, M.: Cure performance of multifunctional monomers to photoinitiators: a thermoanalytical study on bis-GMA-based resins. *J. Mater. Sci.* 26, 3185-3190, 1991.
- 8) Cook, W.D.: Curing efficiency and ocular hazards of dental photopolymerization sources. *Biomater.* 7, 449-454, 1976.
- 9) Cook, W.D.: Spectral distributions of dental photopolymerization sources. *J. Dent. Res.* 61, 1436-1438, 1982.
- 10) Cook, W.D. and Standish, P.M.: Cure of resins based restorative materials. II. White light photopolymerized resins. *Aust. Dent. J.* 28, 307-311, 1983.
- 11) Peuzfeldt, A. and Asmussen, E.: Influence of carboxylic anhydrides on selected mechanical properties of heat-cured resin composites. *J. Dent. Res.* 70, 1537-1541, 1991.
- 12) Hirose, T., Wakasa, K. and Yamaki, M.: Curing performance of visible-light-cured dental resins due to a selectively-filtered visible-light unit. *J. Mater. Sci.* 25, 1214-1218, 1990.
- 13) Urabe, H., Wakasa, K. and Yamaki, M.: Application of multifunctional base monomer to dental composite resins. *J. Mater. Sci. Mater. Med.* 1, 163-170, 1990.
- 14) Yoshida, K. and Greener, E.H.: Effect of photoinitiator on degree of conversion of unfilled light-cured resins. *J. Dent.* 22, 296-299, 1994.
- 15) Chowdhury, N.A., Wakasa, K., Priyawan, R. and Yamaki, M.: Effect of filler content on mechanical strength in bis-GMA-based resins with urethane linkages. *J. Mater. Sci. Mater. Med.* 6, 400-403, 1995.