

Curing performance of visible-light-cured dental resins due to a selectively-filtered visible-light unit

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The spectral distributions of a visible-light curing unit with selectively limited-filters were measured. The results showed that the activation energy for polymerization in an unfilled resin with dimethyl-*p*-toluidine as a reducing agent of tertiary aromatic amine was lower than that in the other unfilled resins and had a larger curing efficiency than the unfilled resins with aliphatic tertiary amines such as dimethylaminoethyl methacrylate and diethylaminoethyl methacrylate and also ketone. The latter amine-containing resins exhibited a larger activation energy compared to the former aromatic tertiary amine-containing resin.

1. Introduction

A photo-sensitizer of camphorquinone (CQ) and a photoreductant affect the properties of resin such as curing efficiency and depth of cure, when different contents and types of CQ and amine are used in the *bis*-GMA/urethane-based resin [1]. The curing efficiency in the visible light (VL)-activated resin is dependent upon light energy for activation [2]. The polymerization of VL-activated composite resins is generally influenced by resin formulation variables (diluent concentration, catalyst type and content) [3, 4].

As dental resins contain the photo-sensitizer CQ which is activated in the wavelength range 400 to 500 nm [5-7], curing depends on the intensity of the radiation when cured by VL in the blue region [5]. The VL activating units with a rigid light tube and a fibre type with a flexible light tube are classified by the design [8, 9]. The peak wavelength in the spectral distributions ranged from 450 to 485 nm for the VL units [10]. Properties of commercial VL units such as the illuminating power and spectral irradiance have been correlated [11-13]. A relation between the degree of conversion and Knoop hardness or strength was sought [3, 14, 15]; however, as a result, the effect of resin formulation on the properties was not clear, despite the fact that a relationship was found for each resin product, because the manufacturers' formulations varied [4, 16]. The temperature of the resin rises during polymerization of the VL-cured composite resin [17-20], the heat effect being considered to be almost due to the light source with a VL curing unit [21]. This temperature rise is considered to be a function of the rate of polymer formation [18, 22].

Recently, Antonucci and Toth [23] have recommended that a differential scanning calorimetry (DSC) method is far less time-consuming. The aromatic tertiary

amines yielded higher curing efficiency than aliphatic tertiary amines in VL-cured composite resins containing 75 wt % barium oxide glass [1]. The average temperature rises were low for VL-cured resins after irradiation with VL units [22, 24]. More detailed study on factors affecting curing characteristics will be necessary. The aims of this study were to (1) examine at which wavelengths and to what degree curing efficiency can be obtained in commercial dental composite resins, using a VL curing unit with selectively-limited filters; (2) determine the curing efficiency of the unfilled resins containing different kinds of reducing agents; and (3) evaluate the activation energy for polymerization.

2. Materials and methods

Two commercial visible-light cured composite resins listed in Table I were tested. The photo-sensitizer such as CQ content, wt %/wt % in the resin phase was analysed (1.02 ± 0.08 for Occlusin; 0.12 ± 0.01 for Silux 5501) [25]. The five 60 wt % *bis*-GMA and 40 wt % TEGDMA-based resin formulations were prepared with commercially available chemicals (*bis*-GMA; 2,2-*bis*[4-(3-methacryloxy-2-hydroxypropoxy) phenyl]propane, (TEGDMA); triethyleneglycol dimethacrylate (TEGDMA) (Table III). The CQO unfilled resin had only CQ without a reducing agent. The unfilled resins were different in reducing agent systems (dimethylaminoethyl methacrylate (DMAEMA), dimethyl-*p*-toluidine (DMPT), diethylaminoethyl methacrylate (DEAEMA) and Michler's

TABLE I The investigated visible-light-cured composite resins

Brand name	Manufacturer	Batch no.	Code
Occlusin	ICI	PH19	OCL
Silux	3M	6L2	SLX

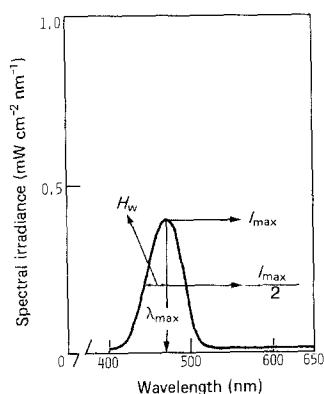


Figure 1 A typical spectral distribution curve of a VL curing unit (λ_{\max} , peak wavelength with a maximum spectral distribution noted by I_{\max} ; H_w , half wavelength width at half I_{\max}).

ketone (MK). The contents of CQ and reducing agent, wt %/wt %, were both 0.5 in the resin phase. The VL curing unit was made to measure each spectrum of visible-light passed through ten special filters (Toshiba Glass Co., Tokyo, Japan; KL-42, 45, 47, 49, 51, 53, 55, 57, 59 and 61) in front of the tungsten halogen lamp (Sylvania EFR; 15V-150 W, Kondo Sylvania Ltd, Tokyo, Japan). The spectrum due to this VL unit was measured by passing the light through a monochromator (Nikon G-250, Tokyo, Japan), according to our recent study [13]. A VL unit of Quick Light (J. Morita Co., Kyoto, Japan) was used with a voltage supply and a light tube. The value of spectral irradiance ($\text{mW cm}^{-2} \text{ nm}^{-1}$) was normalized in a 1 cm^2 area of the fibre-optic tip when the filter was used. Both the peak wavelength at maximum spectral irradiance (peak wavelength λ_{\max}) and the width (H_w ; half of the wavelength showing a half of maximum spectral irradiance (I_{\max})) were analysed as the characteristics of spectral distribution (Fig. 1).

For the VL-activated dental composite resins, listed in Tables I and II, both the curing efficiency and activation energy were evaluated by the VL unit with attached filters for every irradiation. The curing efficiency was measured for the irradiated specimen, similar to our earlier study [13]. The isothermal differential scanning calorimetry (DSC) analysis of unfilled resins (Table II) was performed at 15, 37 and 50°C using the heat output of a VL curing unit (Fig. 2; DT-30; Shimadzu Co., Kyoto, Japan). Each sample was placed in a pre-weighed aluminium sample pan as follows; the pan containing the sample ($5 \pm 0.1 \text{ mg}$) was transferred to the calorimeter cell in DSC unit in Fig. 2, and the measurements were made after 10 min (15°C; isothermal temperature), 5 min (37°C) and 1 min (50°C), checking the stability of the base-line of the DSC curve. The sample weight

TABLE II The unfilled resins studied

Components (wt %)*	Code
0.5% CQ	CQO
0.5% CQ + 0.5% DMAEMA	CMA
0.5% CQ + 0.5% DMPT	CPT
0.5% CQ + 0.5% DEAEMA	CEA
0.5% CQ + 0.5% MK	CMK

* Resin phase; 60 wt % bis-GMA-40 wt % TEGDMA.

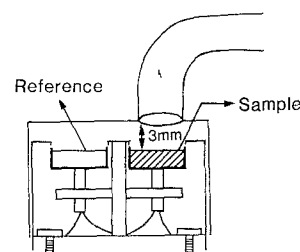


Figure 2 Schematic representation of DSC measurement.

is constant, as the heat output is proportional to the quantity of the sample used [18]. The other aluminium pan empties without a reference weight. After that, the sample was cured at each irradiation time using special filters to produce $\lambda_{\max} = 420, 470$ and 550 nm (see Table III). In this study, each value of integral irradiance calculated from the spectral distribution with different peak wavelengths is described as the value at each value of peak wavelength, at which the selectively filtered spectral distribution is obtained. The variation of heat output rate (mJ sec^{-1}) with time (sec) was obtained on a chart recorder. It is believed that the exothermic heat of reaction could arise from the free radical polymerization of resin monomers [23]. The heat of reaction (cal g^{-1}) is quoted in calories per gram resin used at 37°C, and the maximum heat output rate at a peak height in the DSC curve as $\text{mcal sec}^{-1} \text{ mg}^{-1}$. With DSC measurement it is considered that the maximum heat output rate varies with increasing isothermal test temperature. Using the different maximum heat output rates obtained from the DSC curve, the activation energy for polymerization (Q) is calculated, because the time to reach a peak height is different for different irradiation times (Fig. 6). For the Arrhenius' plot, the rate of heat output is proportionately linear to the exponential of the inverse of isothermal temperature (T_{is}) in the DSC curve which is described as $\exp(-Q/RT_{is})$. In general, the DSC curve has a peak height and a heat of reaction during the curing of the resin [18, 20, 21, 26].

3. Results

According to a typical spectral distribution of the VL curing units shown in Fig. 1, the integral value of irradiance at 470 nm was 24.2 mW cm^{-2} , and 36.0 mW cm^{-2} for 550 nm (Table III). The value was different for the peak wavelengths in spectral

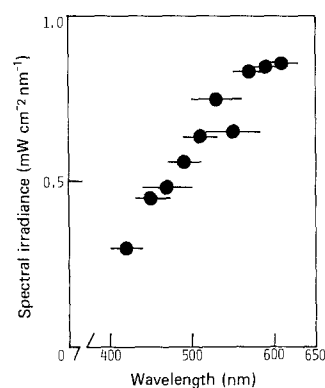


Figure 3 Characteristic of spectral irradiance indicated by λ_{\max} and H_w .

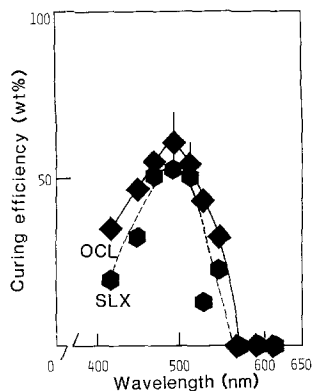


Figure 4 The curing efficiency of VL-activated resins (SLX, Silux; OCL, Occulsin) shown by λ_{\max} using selectively filtered VL curing units.

distribution using different filters, and the irradiance value and irradiation time for each peak wavelength were determined to have the same integral irradiance value as that at 470 nm. The measuring range used was for wavelengths between 400 and 650 nm, because the filters limited the spectral distribution.

Fig. 3 shows each spectral irradiance (I_{\max}) and wavelength width (H_w) obtained from the spectral distribution of the VL curing unit with special filters. The spectral irradiance value increased with increasing peak wavelength. Thus the irradiation time for curing at a larger peak wavelength becomes shorter than that at lower peak wavelength (Table III).

In Figs 4 and 5 the curing efficiency is indicated for commercial dental composite resins (SLX and OCL) and five unfilled resins containing different reducing agents. Silux (SLX) was cured above 50 wt % at both 470 and 490 nm, whereas Occulsin (OCL) had a curing efficiency above 50 wt % for spectral distributions indicating 470, 490 and 510 nm. A significance ($p < 0.01$) was found between materials OCL and SLX for every peak wavelength. In Fig. 5 the curing efficiency was different in the five unfilled resins ranging from about 83 to 0 wt %. A CQO unfilled resin without a reducing agent had the lowest efficiency, ranging from 0.6 to 2.7 wt % in the peak wavelength range between 450 and 490 nm. The maximum value of curing efficiency above 80 wt % was found for a CPT unfilled resin. On the other hand, CMA and CEA unfilled resins had more than 50 wt % curing efficiency between 420 and 510 nm, but the poly-

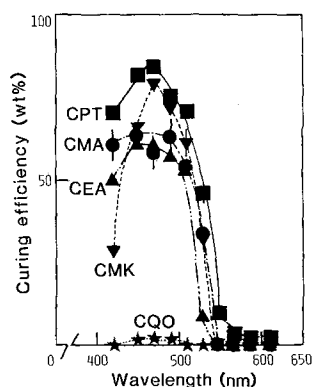


Figure 5 The curing efficiency plotted against λ_{\max} for unfilled resins (CMA, CPT, CEA, CMK and CQO).

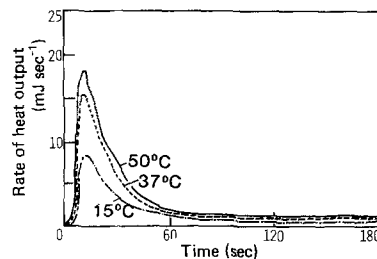


Figure 6 Typical DSC curve of a CMA unfilled resin at isothermal temperatures (15, 37 and 50°C) (filter, KL-47; irradiation time, 10 sec).

merization was not detected above 570 nm. In addition, a CMK resin showed 78.4 wt % curing efficiency at 470 nm, but the value was smaller than for the other resins at 420 nm and above 570 nm, indicating a peak wavelength. A significance was also found in a two-way analysis of variants (materials and wavelength) ($p < 0.01$).

Fig. 6 shows a typical DSC curve of a CMA unfilled resin at 15, 37 and 50°C after being irradiated for 10 sec with a VL curing unit using a KL-47 filter. The heat for polymerization increased on increasing the isothermal temperature from 15 to 37°C, and to 50°C. Fig. 7 shows the relation between the inverse of T_{is} and the logarithm of H (heat output)/ T_p (peak time) in a CMA unfilled resin. From the slope of the line obtained from Fig. 7 the activation energy for polymerization is shown in Figs 8a and b. In a CQO resin the value of activation was not obtained for 420 and 550 nm (peak wavelength), but the value at 470 nm was 1.0 kcal mol⁻¹ (Fig. 8a). The unfilled resins (CEA, CMA, CMK, CPT) containing reducing agents had values of 2.8 to 4.3 kcal mol⁻¹ at 420 nm. The largest activation energy was obtained at a larger peak wavelength than 420 nm in CEA, CMA and CMK unfilled resins. The CPT resin had a larger curing efficiency and lower activation energy for polymerization using a filter of 470 nm peak wavelength (Fig. 8b). At almost the same curing efficiency as the CPT unfilled resin, the other resins containing reducing agents (CEA, CMA, CMK) needed larger activation energies during polymerization.

4. Discussion

The VL curing unit used showed typically spectral distributions in the wavelength range 400 to 650 nm

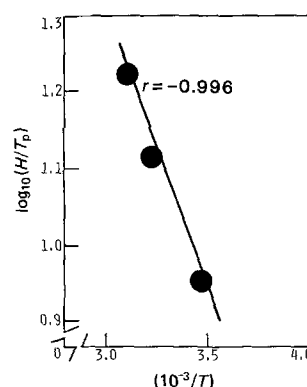


Figure 7 Arrhenius' plot for the unfilled resin (CMA) obtained from Fig. 6.

TABLE III Characteristics of visible-light curing unit with selectively-limited filters (the irradiation time was selected to equal the value for integral irradiance)

	λ_{\max} (nm)									
	420	450	470	490	510	530	550	570	590	610
Irradiance (mW cm^{-2})	18.1	22.5	24.2	33.6	39.3	44.6	36.0	47.3	48.2	51.3
Irradiation time (sec)	13	11	10	7	6	5	7	5	5	5

(Fig. 1). The spectral distributions of irradiance were normally in a 1 cm^2 area of the tip [13, 27] because the VL unit varied significantly in the cross-sectional area of the fibre-optic tip of the light guide [18]. The peak of spectral irradiance was in the wavelength range 400 to 650 nm with reference to the spectral irradiance/wavelength profile in terms of different VL units [5, 6, 11, 13]. Distinct differences were found in the spectral irradiance when different peak wavelengths and irradiation times were used (Fig. 3), ranging from 0.25 to 0.80 ($\text{mW cm}^{-2} \text{ nm}^{-1}$) (Table II). Therefore, the characteristics of spectral irradiance were analysed (Fig. 1), and the combination of irradiance and irradiation time for each special filter was obtained to polymerize the commercial dental composite resins (OCL and SLX; Table I) and five different unfilled resins (Table II) at the same integral irradiance (Table III). The curing efficiency for each peak wavelength increased for wavelengths 470, 490 and 510 nm for the commercial dental composite resins (Fig. 4). The absorption spectrum of the photo-sensitizer (CQ) was observed in the wide wavelength range 350 to 520 nm, and ineffective wavelengths occurred at $< 410 \text{ nm}$ and $> 500 \text{ nm}$ [5]. For two commercial resins such as Occulsin (OCL) and Silux (SLX), the effective wavelengths for polymerization were widespread at such peak wavelengths 410, 510, 520 and 530 nm when filters were used. In the previous study [5], the influence of CQ or reducing agent on the curing efficiency was not clarified, because the CQ content and the kind of reducing agent were not obvious. The VL curing units showed the greatest irradiance near the wavelength region 460 to 480 nm [5, 6, 8]. For a CQO unfilled resin (CQ; 0.5 wt % without a reducing agent) the polymerization of the resin occurred with about 2 wt % curing efficiency at 470 nm peak wavelength (Fig. 5). On the contrary, wider wavelengths to polymerize unfilled resins (CMA, CPT, CEA, CMK) than the CQO unfilled resin were found, and also a larger curing efficiency

than that of the CQO unfilled resin was detected. Of the unfilled resin containing reducing agents the CPT unfilled resin had the largest value at 470 nm. At other wavelengths, the CPT unfilled resin had a larger value of curing efficiency than the other unfilled resins.

Only the CPT unfilled resin contains DMPT which is an aromatic tertiary amine, although the CMA, CEA and CMK unfilled resins do contain reducing agents such as an aliphatic tertiary amine and ketone. Figs 8a and b show the effect of reducing agents (CQ(wt %); 0.5) on the activation energy for polymerization. Despite the fact that the CQ content in the resin phase is constant for the unfilled resin, the CPT unfilled resin had the lowest values of activation energy of all the unfilled resins containing reducing agents, ranging from 1.7 to 9.1 kcal mol^{-1} above 470 nm, whereas the activation energy for unfilled resins (CEA, CMA, CMK and CPT) was below 5.0 kcal mol^{-1} when selectively filtered at 410 nm (Fig. 8a). With a 470 nm selective filter (Fig. 8b) the unfilled resins such as CEA, CMA and CMK had larger activation energies (3.4 to 5.4 kcal mol^{-1}) than that (1.7 kcal mol^{-1}) of a CPT unfilled resin. At almost the same value of curing efficiency the activation energy for polymerization of the CPT unfilled resin was the lowest of all the unfilled resins investigated. On low-temperature (room temperature) polymerization of acrylic resins [28] the aromatic amines were greatly superior to the aliphatic amines with respect to the ability to accelerate polymerization. The aromatic amines yielded a higher curing efficiency and depth of cure than aliphatic amines in the *bis*-GMA/urethane composite resins (CQ 0.15 wt %; barium oxide glass filler 75 wt %) [1]. DMAEMA (an aliphatic tertiary amine) is regarded as a typical reducing agent [30]. DMPT is an accelerator for the self-curing resins [29, 31]. DEAEMA, as a reducing agent, was found to be contained in one brand (Silux 5501, an old one previously sold) [32]. According to the patent information, MK is ketone [33]. On adding 0.5 wt %

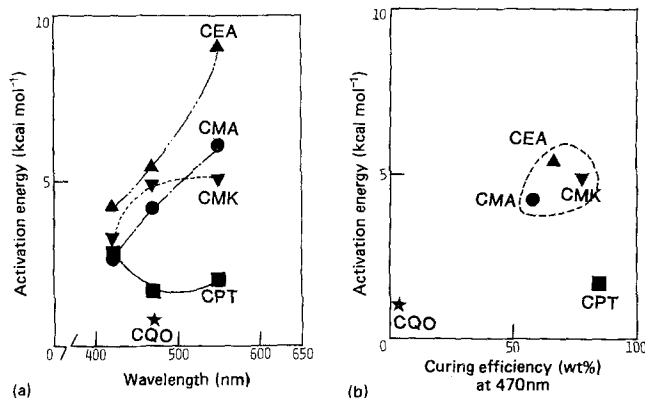


Figure 8 Activation energy for polymerization plotted against (a) wavelength, and (b) curing efficiency in all unfilled resins investigated.

reducing agent to a CQO resin in the resin phase, the unfilled resins containing reducing agents showed a larger curing efficiency (Fig. 8b). This means that CQ is elevated more efficiently to the triplet state, such as the formation of radicals, in the presence of a reducing agent.

The present study clarified which reducing agents were more suitable for CQ contained in dental composite resins. It has not, however, clarified what quantity of a reducing agent is optimal for CQ activation. The study also clarified that the addition of reducing agents only to CQ-containing unfilled resins increased the curing efficiency. In a reducing agent, such as DMPT, the smallest activation energy for polymerization was found among the reducing agents used. This supports the fact that the aromatic amine is activated more easily than the aliphatic amines and the ketone.

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