Effect of various visible light photoinitiators on the polymerization and color of light-activated resins

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The purpose of this study was to investigate effects of various visible light photoinitiators on the polymerization efficiency and color of the light-activated resins. Four photoinitiators, including camphorquinone, phenylpropanedione, monoacrylphosphine oxide (TPO), and bisacrylphosphine oxide (Ir819), were used. Each photoinitiator was dissolved in a Bis-GMA and TEGDMA monomer mixture. Materials were polymerized using dental quartz-tungsten halogen lamp (QTH), plasma-ark lamp and blue LED light-curing units, and a custom-made violet LED light unit. The degree of monomer conversion and CIE $L^*a^*b^*$ color values of the resins were measured using a FTIR and spectral transmittance meter. The degree of monomer conversions of TPO- and Ir819-containing resins polymerized with the violet-LED unit were higher than camphorquinone-containing resin polymerized with the QTH light-curing unit. The lowest color values were observed for the TPO-containing resin.

Our results indicate that the TPO photoinitiator and the violet-LED light unit may provide a useful and improved photopolymerization system for dental light-activated resins.

Keywords: Light-activated resin, Photoinitiator, Color

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INTRODUCTION

Visible light-activated composite resins polymerized with the use of a light-curing unit (LCU) are widely used in dentistry as direct filling restorative materials because of their easy handling, aesthetics, and improved physical and mechanical properties. Considering the adverse biological effects of UV light¹⁾, the use of camphorquinone (CQ) as a photoinitiator has been largely accepted in dentistry, because it absorbs wavelengths in the visible blue-light region. However, CQ has some drawbacks such as low polymerization efficiency, which results in low mechanical properties of the resin, as well as the possible toxic effects of residual monomers^{2,3)}. Additionally, CQ is a solid yellow compound with an unbleachable chromophore group, and thus a large amount of CQ in the resin formulation leads to undesirable yellowing of the final polymerized resin⁴⁾. This places practical limits on the acceptable concentration of CQ in the resin. The light absorption requirements of CQ should correlate with the spectral emission profile of the dental LCU, and dental quartz-tungsten halogen (QTH) and xenon plasma-arc lamp (PAC) LCUs, filtered to provide light wavelengths between about 400 and 500 nm, have been optimized for the light absorbance characteristics of CQ⁵⁻⁷⁾. An absorbance wavelength in the visible light region is desirable for a photoinitiator of light-activated resin, because visible light has few biological effects on tissues other than the retina. Recently, a blue light emitting diode (B-LED) LCU has begun to be adopted for polymerizing dental light-activated resins. In comparison with the QTH and PAC LCUs, the B-LED LCU offers longer lifetime with less degradation, a

more homogeneous output of radiated light owing to its simple light passes, and energy savings⁸⁻¹²⁾.

To overcome the drawbacks of CQ, some alternative photoinitiators have been introduced for dental light-activated resins as the photoinitiators, which have desirable benefits such as a lower yellowing effect and higher polymerization efficiency compared with CQ. Some studies recommended phenylpropanedione as a promising alternative system for dental adhesives and resins^{2,13-15)}. Other studies indicated that monoacrylphosphine oxide could replace CQ without diminishing the properties of resin¹⁶⁾. The bisacrylphosphine oxide was also introduced as a possible photoinitiator system¹⁷⁾. However, most of the studies used conventional QTH LCUs for polymerization of resin. Since light absorbance wavelengths of the alternative photoinitiators were different from those of CQ, light-activated resin containing alternative photoinitiators may not be efficiently polymerized when using conventional dental LCUs, such as QTH, PAC and LED LCUs, that have been optimized for absorbance wavelengths of CQ. Moreover, few information is available on the color effect of alternative photoinitiators except for phenylpropanedione^{13,15)} on aesthetics of resin polymerized with dental LCUs in comparison with that of CQ.

The purpose of this study was to investigate the efficacy of alternative various visible light photoinitiators on the polymerization of light-activated resin polymerized using different dental LCUs and a custom-made violet LED (V-LED) light unit. In addition, the color effects of the alternative photoinitiators on the light-activated resin were compared to that of CQ.

MATERIALS AND METHODS

Experimental light-activated resins

Four photoinitiators, phenylpropanedione (PPD, Kanto Chemical, Tokyo, Japan), monoacylphosphine oxide (TPO, DAROCUR TPO, Ciba Specialty Chemical, Basel, Switzerland), bisacylphosphine oxide (Ir819, IRGACURE 819, Ciba Specialty Chemical), and camphorquinone (CQ, Wako Pure Chemical Industries, Osaka, Japan) were used in this study, as shown in Table 1. Each photoinitiator (1.5 wt%) was dissolved in a Bis-GMA (50 mol%, Polysciences, Warrington, PEN, USA) and TEGDMA (50 mol%, Wako Pure Chemical Industries) monomer mixture along with ethyl p-dimethylamino benzoate (0.2 wt%, Nacalai Tesque, Kyoto, Japan) as a reducing agent.

Light absorbance characteristics

The light absorbance characteristics of the four photoinitiators were determined using a spectral transmittance meter (TM-1, Topcon, Tokyo, Japan). Each photoinitiator was dissolved in ethanol and poured into a stainless steel mold with a cylindrical hole ($\phi 10 \times 1.0$ mm) set on a thin glass plate (0.15 mm thickness) and covered by a thin glass plate. Measurements were recorded from 380 to 500 nm in

the visible light region, at 5-nm intervals. The light absorbance (A) of the specimen was calculated as the ratio of the intensity of the incident light (I_0) to the intensity of the transmitted light (I) passing through the specimen at each wavelength, using the equation; $A = \log_{10}(I_0 / I)$.

LCUs

Specimens for measurements were polymerized using dental QTH, PAC, and B-LED LCUs and a custom-made V-LED light unit listed in Table 2, together with specification, code and manufacture. The dental LCUs were selected as representatives of commercially available dental LCUs with different light sources. The QTH (Jetlite 1000, J. Morita USA, Tustin, CA, USA) LCU contained a 75-W quartz-tungsten halogen reflector lamp and a band-pass optical filter to limit temperature-increasing wavelengths in a hand piece. The PAC (Credi II, 3M Health Care, Tokyo, Japan) LCU was equipped with a 300-W xenon plasma-arc reflector lamp and a band-pass filter. The B-LED (Jetlite 5000, J. Morita USA) LCU contained a high-power 5-W blue-LED ($\phi 6$ mm) in a hand piece. The irradiation times were 30 seconds for the QTH and B-LED LCUs, and 10 seconds for PAC LCU, according to the manufacturers' recommendations. The custom-

Table 1 Photoinitiators used in this study

Photoinitiator		Code
dl-2,3-diketo-1,7,7-trimethylnorcamphane		CQ
1-phenyl-1,2-propadione		PPD
2,4,6-trimethylbenzoyl-diphenylphosphine oxide		TPO
Bis(2,6-dichlorobenzoyl)-(4-propylphenyl)phosphine oxide		Ir819

Table 2 Light-curing units used for polymerization in this study

Light-curing unit	Use	Code	Light source	Irradiation time (seconds)	Manufacture
Jetlite 1000	clinical	QTH	quartz-tungsten halogen lamp	30	J. Morita USA
Credi II	clinical	PAC	xenon plasma-arc lamp	10	3M Health Care
Jetlite 5000	clinical	B-LED	blue-LED	30	J. Morita USA
Violet LED	custom-made	V-LED	violet-LED	60	–

Fig. 1 Schematic representation of the custom-made V-LED light unit.

made V-LED light unit contained two parallel connection gallium nitride violet LEDs ($\phi 8$ mm, OSSV8131A, Opto Supply International, Hong Kong, China) used in video-disc technology as shown in Fig. 1. The LEDs operated at a current of 25 mA and voltage of 5 V with a power dissipation of 200 mW. The LEDs were driven by a modulation circuit produced for this study¹⁸. The light from the LEDs was concentrated with a built-in polymer lens, which focused the light through a circular footprint and directed it toward the resins. The V-LED irradiation time was 60 seconds of its relatively low light power.

Radiation characteristics

The radiation characteristics of the light emitted by each LCU were determined using a monochromator (CT-10, JASCO, Tokyo, Japan) and a laboratory-grade optical power meter with a photo-diode detector (TQ-8210 and -82017, Advantest, Tokyo, Japan). The light from the LCU was incident on the monochromator, and the monochromatic light intensity, measured by the power meter was recorded from 380 to 500 nm, at 5-nm intervals. The spectral flux represents the optical power output, in $\mu\text{W}/\text{cm}^2$, from the LCU at each given wavelength. The temperature increase due to the light from the LCU was monitored using a digital thermometer with a thermocouple (HPD-2123 and E-J1-M1, Anritsu Meter, Tokyo, Japan), set 5.0 mm from the center of the dental LCUs and the custom-made V-LED, at room temperature and was documented using a recorder.

Degree of monomer conversion

The degree of monomer conversion after polymerization was measured by Fourier transformation infrared spectroscopy (FTIR, FT/IR-460, JASCO), and was determined from the aliphatic and aromatic C=C peaks

for unpolymerized and polymerized resin¹⁹. For unpolymerized resin, a small amount of resin monomer was placed between two KBr disks, and the spectrum was recorded in transmission mode over the range of 4,000 to 400 cm^{-1} at a resolution 1 cm^{-1} . To polymerize the monomers, resin was poured on a glass plates, covered by a thin glass plate, using spacers to maintain the space between the glass plates; and then irradiated. After polymerization, specimens ($\phi 10$ mm $\times$ 150 μm) were prepared from the polymerized material and were scanned by FTIR. The remaining unconverted double bonds were determined by comparing the ratio of the aliphatic C=C absorption peak at 1637 cm^{-1} to the aromatic C=C peak at 1608 cm^{-1} between polymerized and unpolymerized specimens. The absorption of the aromatic C=C stretching band served as an internal standard, as it remains constant during the polymerization reaction. The monomer conversion was determined by subtracting the percentage of residual aliphatic C=C bonds from 100%.

Color measurement

The resin monomer was poured into a stainless steel mold ($\phi 10 \times 1.0$ mm) and covered by a thin glass plate. Light from the QTH LCU was used to irradiate the resin for 30 seconds. The color value of the resin, on the CIE $L^*a^*b^*$ color system, was determined before and after polymerization by measuring the transmitted light through the specimen, using the spectral transmittance meter (TM-1). The L^* is the lightness coordinate, and the a^* and b^* describe the chromaticity on the red-green axis and yellow-blue axis, respectively. As a^* becomes more positive in value, the color is more red; as a^* becomes more negative in value, the color becomes more green. As b^* becomes more positive in value, the color is more yellow; as b^* becomes more negative in value, the color becomes more blue. The color values were used to calculate color difference ΔE^* that occurs during polymerization using the equation; $\Delta E^* = [(\Delta L^*)^2 + (\Delta a^*)^2 + (\Delta b^*)^2]^{1/2}$, where ΔL^* , Δa^* and Δb^* are the changes in L^* , a^* and b^* between before and after polymerization.

All specimens were stored in air at 37°C for 24 hours before testing.

Statistical analysis

Multiple comparison of the values of the degree of monomer conversion and the color values among materials were made using one-way analysis variance and Tukey's test with a significance level of $p = 0.05$. Five specimens of each material were used for each test.

RESULTS

The light absorbance wavelength spectra of the four photoinitiators are shown in Fig. 2. All photoinitiators had absorption wavelengths in the visible light wavelength region. CQ and PPD showed a broad absorbance wavelength distribution from 380 to 500

Fig. 2 Light absorbance spectra of four photoinitiators between wavelengths from 380 to 500 nm.

Fig. 4 Variation of the temperature increase of radiation light during each irradiation time of three dental LCUs and the custom-made V-LED light unit.

Fig. 3 Radiation light spectra of three dental LCUs and the custom-made V-LED light unit between wavelengths from 380 to 500 nm.

Fig. 5 Comparison of the degree of monomer conversion of the resin containing four photoinitiators polymerized with three dental LCUs and the custom-made V-LED light unit. Same capital letters indicate no statistically significant differences.

nm. TPO and Ir819 showed significantly greater light absorption at shorter wavelengths than CQ and PPD. The light absorbance values at peak wavelength were 0.14 for CQ, 0.56 for PPD, 2.1 for TPO, and 2.3 for Ir819.

Figure 3 presents the wavelength spectra for light radiated from the four LCUs. The QTH LCU emitted a broad wavelength spectrum, from 380 to 500 nm in the visible-light region, with a peak at around 465 nm. Similarly, the PAC LCU showed a spectrum in the region from 420 to 500 nm with peaks at around 470 and 490 nm. The B-LED LCU emitted light within a narrow band from 420 to 500 nm, with a peak at around 460 nm. The spectrum of light radiated by the V-LED light unit was a narrow band between 390 and

430 nm, with a peak at around 410 nm and a half-band width of about 25 nm. The intensities of the radiated light at peak wavelength were $68.0 \mu\text{W}/\text{cm}^2$ for QTH, $148.4 \mu\text{W}/\text{cm}^2$ for PAC, $137.1 \mu\text{W}/\text{cm}^2$ for B-LED LCUs, and $9.5 \mu\text{W}/\text{cm}^2$ for V-LED light unit. Figure 4 shows the temperature increase due to radiated light for each LCU at the end of the radiation time. The temperature increased with increasing radiation time. The maximum temperature increases were 12.6°C for QTH, 15.4°C for PAC, 16.0°C for B-LED LCUs, and 1.6°C for V-LED light unit.

The degree of monomer conversion in the resin containing each of the four photoinitiators polymerized with each of the four LCUs is shown in Fig. 5. The CQ- and TPO-containing resins could not be

Table 3 Color values before and after polymerization, and color difference during polymerization of the resins containing four photoinitiators

Photoinitiator	Color value				Color difference during polymerization
	before polymerization		after polymerization		
	a^*	b^*	a^*	b^*	
CQ	−3.9 (0.1)	13.1 (0.1)	−2.3 (0.1) ^a	7.8 (0.3) ^b	6.2 (0.8) ^c
PPD	−9.8 (0.3)	21.2 (0.9) ^A	−10.4 (0.1)	21.9 (0.4) ^A	1.2 (0.6)
TPO	−2.1 (0.1) ^B	1.2 (0.1)	−2.0 (0.2) ^{B,a}	3.4 (0.1)	2.8 (0.2)
Ir819	−7.5 (0.1)	11.3 (0.1)	−3.9 (1.2) ^a	6.8 (1.1) ^b	5.8 (1.2) ^c

Mean value of five specimens with SD in parentheses. Same capital letters in same row indicate no statistically significant differences between a^* or b^* values before and after polymerization, and same lowercase letters in same column indicate no statistically significant differences.

polymerized with the V-LED LCU, and B-LED light unit, respectively. The polymerization percentage varied, depending on the combination of photoinitiator and light source, over the following ranges: 64.8% for CQ- to 75.7% for TPO- containing resin and the QTH LCU, 51.3% for TPO- to 58.1% for Ir819-containing resin and the PAC LCU, 65.4% for PPD- to 68.8% for CQ-containing resin and the B-LED LCU, and 61.4% for PPD- to 77.5% for Ir819-containing resin and the V-LED light unit.

The color values of the polymerized resins are shown in Table 3. The a^* and b^* values reflect the chromatic component of the resin. The PPD-containing resin showed significantly higher absolute a^* value in green shift and b^* value in yellow shift, compared with the resins containing the other photoinitiators. The lowest absolute values of a^* and b^* were observed for the TPO-containing resin before and after polymerization. CQ showed higher color difference during polymerization than the other photoinitiators.

DISCUSSION

Dental light-activated resins that absorb visible light of about 380 and 500 nm are desirable in order to avoid the harmful biological effects of UV light and the heating effect of IR light. Although different from those of CQ, the wavelengths of light absorbed by PPD, TPO, and Ir819 were in the visible region, between 380 and 500 nm (Fig. 2). For TPO and Ir819, significant light absorbance was observed at wavelengths of up to 420 and 440 nm, respectively. PPD showed almost the same light absorbance as CQ at 470 nm, which is the light absorbance peak of CQ. The light absorption characteristics of the photoinitiators were closely related to their effects on resin polymerization and thus could be used as parameters for determining the polymerization efficiency of a resin⁽⁴⁾. The values of the light absorption by PPD, TPO, and Ir819 at peak wavelength reached 4.0 to 16.4 times that of CQ. This indicates that the use of PPD, TPO, and Ir819 as visible light photoinitiators for dental light-activated resin would confer significantly higher polymerization

efficiency, in comparison with CQ.

To achieve adequate polymerization of a light-activated resin, the light absorption spectrum of the photoinitiator should fully or partly overlap the radiation spectrum of the dental LCU used for photopolymerization (Fig. 3). The QTH and PAC LCUs emitted light within a wide wavelength band, from 380 to 500 nm, which overlaps the absorption spectra of all the photoinitiators used in this study. The narrow band of radiated light, with a peak at 460 nm, produced by the conventional dental B-LED LCU does not practically overlap the absorption wavelength range of TPO. On the other hand, the custom-made V-LED light unit emitted visible violet light of 390 to 430 nm with a peak at around 410 nm, which is approximately 60 nm less than the peak obtained with the B-LED LCU. Thus, the wavelength range of the light radiated by the V-LED light unit is suited for the absorption wavelengths of all the photoinitiators except CQ.

Although all of the resins containing photoinitiators were polymerized when irradiated with the QTH LCU, the monomer conversion rates of the TPO- and Ir819-containing resins were significantly higher than those of the CQ- and PPD-containing resins, despite the relatively low light intensity of the QTH LCU at shorter wavelengths (Fig. 5). Significantly greater light absorbance by TPO and Ir819 might have initiated a higher degree of monomer conversion; CQ also absorbed light of around 400 nm, but its light absorbance at wavelengths less than 430 nm was significantly less than that of the other photoinitiators. All of the resins that were polymerized using the PAC LCU exhibited degrees of monomer conversion that were lower than those with the QTH LCU⁽⁷⁾. The custom-made V-LED light unit could not produce polymerization of the CQ-containing resin, owing to the short and narrow wavelength band of the light radiated from the V-LED light unit. However, the PPD-, TPO-, and Ir819-containing resins were polymerized with the V-LED light unit to almost the same degree of monomer conversion as that achieved with the QTH LCU, even through the V-LED light unit displays only one-fourth the power of the light radiated from the QTH LCU at

the peak wavelength of 410 nm. Although other study¹⁶⁾ reported that experimental bonding materials containing TPO as photoinitiator were sufficiently polymerized with a dual-wavelength LED light unit with peak wavelengths at 370 and 530 nm, the peak wavelength was below 390 nm of UV light. This indicates that the V-LED light unit can achieve sufficient polymerization of resins containing visible-light photoinitiators substituted for CQ.

CQ causes an undesirable yellowish discoloration of the resulting aesthetic resin and compromises the color match to the teeth. Therefore, from the standpoint of aesthetics, an alternative photoinitiator should improve the yellowing effect on the resin. There were significant differences in the color values among the resins containing the four photoinitiators (Table 3). The PPD-containing resin showed the highest values of a^* and b^* , and the Ir819-containing resin also exhibited relatively high color values, similar to those of the CQ-containing resin. Thus, although both photoinitiators exhibited higher photopolymerization efficiency than CQ, no improvement in the yellowing effect was observed. By comparison, the TPO-containing resin showed significantly lower color values, especially b^* values (yellow-blue axis), than the CQ-containing resin both before and after polymerization. Moreover, although the color difference during polymerization of the TPO-containing resin was more than two units, it was only almost half of that of the CQ-containing resin and considered the minimum color change that could not be easily detected visually by the naked eye²⁰⁾. Given the higher polymerization efficiency of TPO compared with CQ, a lower concentration of TPO would be required, further lessening the color effect and discoloration during polymerization without reducing the degree of polymerization. These results indicate that in comparison with CQ, the use of TPO as a photoinitiator may achieve greater improvement in the aesthetic appearance of light-activated resin.

Based on the measured degree of monomer conversion, TPO-containing resin can be efficiently polymerized using either the dental QTH LCU, with a wide-band spectrum of 380 to 500 nm, or the V-LED light unit, with a narrow-band spectrum of 390 to 430 nm. However, the light radiated from the QTH LCU caused significant temperature increases during irradiation (Fig. 4). Another study reported that a critical intrapulpal temperature increase occurs when photocuring with dental LCUs with all light sources, including LEDs³⁾. The biological effects of these temperature increases are not completely known, but it has been suggested that a temperature increase of more than 5.5°C within the pulp can lead to irreversible damage²¹⁾. The most significant source of heat during the polymerization of a light-activated restorative derives from the LCU and not the restorative material²¹⁾. Temperature increases in excess of 5.5°C may occur in clinical situations when a QTH LCU is used to polymerize light-activated resin, and the resultant high temperature may cause negative

consequences for tooth health. In contrast, the V-LED light unit exhibited a temperature increase of only 1.6°C, even after a 60 seconds irradiation; this is significantly lower than the increases with other dental LCUs. The short wavelengths of the violet-light from the V-LED light unit would minimize the heat generated, compared with the heat resulting from the longer-wavelength of conventional dental LCUs. Moreover, power dissipation of the V-LED is only almost 4.0% of that of conventional high-power B-LED. The power dissipated becomes lower, heat generated in the LED is more minimized. As the heating of a tooth should be avoided, the low heat produced in association with the V-LED light unit would make it useful and desirable as a dental LCU for clinical use. Moreover, the V-LED light unit emitted no light below 390 nm, precluding the harmful biological effects of UV light.

Our results indicate that TPO, owing to its low color effect and high polymerization efficiency, and the V-LED light unit, owing to its visible light radiation and very low heating effect, may provide an improved photopolymerization system for dental light-activated resin.

CONCLUSION

The present study demonstrated that PPD-, TPO-, and Ir819-containing resins polymerized with a custom-made V-LED light unit had approximately the same or higher degree of monomer conversion, in comparison with that of CQ-containing resin polymerized with a dental QTH LCU. The V-LED light unit exhibited low temperature increase during light irradiation. The TPO-containing resin showed absolute a^* and b^* color values significantly lower than those of the resins containing the other photoinitiators. The TPO-containing resin also showed less of a color change during polymerization, compared with CQ-containing resin. Thus, the TPO photoinitiator and the V-LED light unit, which exhibits very low temperature increase during light irradiation, may provide a useful and improved photopolymerization system for dental light-activated resins.

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