Hybrid UV LED Device for Simulating Spectrum of High-Pressure Mercury Lamp: Evaluation in UV Curing Process

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A hybrid ultra-violet light emitting diode (UV LED) comprising short and long wavelength UV LEDs (310, 340, and 365 nm) was developed and compared with the high-pressure mercury lamp for UV curing of a mixture of diurethane dimethacrylate, 1-hydroxy-cyclohexyl phenyl ketone, and diphenyl (2,4,6-trimethylbezoyl) phosphine oxide. The curing ability of the hybrid UV LED combinations was evaluated by comparing the thickness of the un-polymerized layer, calculated from the mass before and after rinsing the UV-cured film under air. The results indicated that among the combinations of UV LEDs, the combination of 365 nm and 310 nm UV LEDs provided the thinnest un-polymerized layer. This result was comparable to that obtained with the high-pressure mercury lamp. Nevertheless, the thickness of the un-polymerized layer achieved with the high-pressure mercury lamp was less than that with any of the UV LED combinations. The data show that the 405 nm line of the high-pressure mercury lamp functions to photopolymerize the monomer and is indispensable for the UV curing process.

Keywords: UV LED, High-pressure mercury lamp, Oxygen inhibition

1. Introduction

The high-pressure mercury lamp is the standard photon source used in industrial UV curing processes. However, it uses mercury, which is harmful to the human body and other organisms. Thus, replacing the mercury lamp with an ultraviolet light emitting diode (UV LED) is a promising alternative [1].

For UV LEDs to gain prominence, their UV curing performance must be comparable to that of the classical high-pressure or medium-pressure mercury lamps. Okamura et al. presented the optimal formulation of monomers and photoinitiators for use with UV-C LEDs (265, 285, and 300 nm peaks) and pointed out that the UV-C LED is effective for addressing oxygen inhibition for UV curing of resins under air [2]. Taki et al. compared the network structures formed by the high-pressure mercury lamp and 365 nm UV LED. Considering the kinetic constants and kinetic chain length, the network structures differed on the basis of the photon source [3]. Karasu et al. investigated the effect of a UV absorber in the UV curable resin on the UV curing performance at the surface [4]. Cationic photopolymerization with the mercury and UV LED lamps was also evaluated [5]. Organozirconium was studied as a radical scavenger to enhance the surface UV curing using the mercury lamp and UV LED lamps [6].

Moreover, photoinitiators specialized for UV LEDs and visible-light LEDs have been developed for 3D printing applications [7–11]. For dental restoratives, UV curable resin composites activated by UV LEDs or blue LEDs have been designed [12]. Most studies used a single-peak UV LED as the light source. Investigation of the simultaneous use of different wavelength UV LEDs for resin curing has not been performed.

UV curable resins optimized for the high-pressure mercury lamp require short-wavelength as
well as long-wavelength UV light given that the mercury lamp has several peaks. From the industrial viewpoint, changing the formulation of the resins to optimize curing with a single-peak UV LED while maintaining the final physical properties, e.g., hardness, durability, clarity, etc., is a challenge. Instead of changing the composition of the UV curable resin for use with UV LEDs, the UV LEDs must meet the demands of existing UV curable resins.

The objective of this study is to simulate the spectrum of the high-pressure mercury lamp by using a hybrid UV LED and to verify the equivalence of the quality of the products cured with the UV LED versus that cured with the high-pressure mercury lamp. A hybrid UV LED that simultaneously emits long-wavelength (365 nm) and short-wavelength (300 and 340 nm) UV light from one light source is designed and evaluated.

2. Experimental

2.1. Materials

A mixture of diurethane dimethacrylate (DUDM, Sigma-Aldrich), 1-hydroxycyclohexyl phenyl ketone (HCK, Irgacure 184, BASF), and diphenyl(2,4,6-trimethylbezoyl)phosphine oxide (TPO, Irgacure TPO, BASF) in a 98:1:1 weight ratio was used as the UV-curable resin. The mixture was stirred at ca. 23 °C and stored for at least 24 hours to increase the homogeneity.

2.2. UV light source

A high-pressure mercury lamp (OmniCure S2000, ExFo, Canada) was used as a light source for comparison with the hybrid UV LEDs consisting of combinations of three different UV LEDs. The location of UV LEDs was optimized to get flat light intensity distribution by the luminance simulator (LightTools, Synopsys, Inc). The composition of the UV LEDs is shown in Table 1. The UV LEDs were assembled as shown in Fig. 1.

The UV intensity was measured using a photometer (UIT-150, Ushio, Japan) with maximum sensitivity at 365 nm. The emission of each UV LED was adjusted to simulate the spectrum of the high-pressure mercury lamp. First, the intensity of the UV emission of the high-pressure mercury lamp was set at 3.63 mW cm⁻² by adjusting the iris and distance to the photosensor. Thereafter, all of the UV LEDs were activated and the intensity of the respective emissions was adjusted to achieve the desired spectral profile. Finally, the distance to the photosensor was adjusted to achieve the desired UV intensity at 365 nm.

Figure 2 shows the hybrid UV LED device, sample stage, lens, and optical fiber of the spectrometer.

The three different UV LED lamps reproduced six peaks in the spectral profile of the high-pressure mercury lamp, but not the peak at 405 nm. The molar absorption coefficients of the photoinitiators are shown in Fig. 3. The combined emission spectrum of the UV LEDs covers the absorptions of the photoinitiators.

![Fig. 1. Location of UV LEDs on the circuit board and image of hybrid UV LED device.](image)

![Table 1. Specifications of UV-LEDs.](image)

| UV LED   | LED365 | LED340 | LED310 |
|----------|--------|--------|--------|
| Peak λ [nm] | 365  | 340  | 310  |
| Radiant flux (mW) | 1450 | 30  | 30  |
| Supplier | Nichia | DOWA  | Nikkiso |
| Catalogue name | NVSU233B | UF4XU  | VPS1A1 |
| Number of bulbs | 1 | 4  | 4  |

![Fig. 2. Schematic of the hybrid UV LED device, sample stage, lens, and high-pressure mercury lamp.](image)

![Fig. 3. (a) Molar absorption coefficients of TPO and HCK, and (b) spectra of high-pressure mercury lamp (Hg) and hybrid UV LED (UV LED).](image)
Table 2. Design of experiments.

| Exp. | 310 nm | 340 nm | 365 nm | Hg | Max. Int. [mW cm$^{-2}$]* | Number of runs | Thickness of un-cured film [μm] |
|------|--------|--------|--------|----|--------------------------|----------------|-------------------------------|
| 1    | ON     | ON     | ON     |    | 3.63                     | 4              | 14.6                          |
| 2    | ON     |        | ON     |    | 2.61                     | 4              | 12.9                          |
| 3    |        | ON     | ON     |    | 3.62                     | 5              | 18.0                          |
| 4    | ON     |        |        |    | 1.12                     | 4              | 16.3                          |
| 5    |        |        | ON     |    | 2.58                     | 3              | 18.4                          |
| 6    | ON     |        |        |    | 1.06                     | 3              | 26.0                          |
| 7    | ON     |        |        |    | 0.07                     | 3              | 16.6                          |
| 8    |        | ON     |        |    | 3.63                     | 3              | 11.7                          |

*Maximum intensity measured with the photosensor having maximum sensitivity at 365 nm.

2.3. Evaluation

The performance of the hybrid UV LED was evaluated on the basis of the thickness of the cured film after UV irradiation. The UV curable resin was spun-cast on 2 × 2 cm silicon wafer and cured with either the high-pressure mercury lamp or the hybrid UV-LED for 1 min under air. The cured film was rinsed with isopropanol and the weight-loss was measured to calculate the thickness of the un-cured film, $L$:

$$L = L_{Si} \frac{\rho_{Si}}{\rho_{resin}} \frac{M_0 - M_1}{M_{Si}}$$

where $L_{Si}$ is the thickness of the silicon wafer; $\rho_{Si}$ and $\rho_{resin}$ are the density of silicon and the resin, respectively; $M_0$ and $M_1$ are the overall mass before and after rinsing; $M_{Si}$ is the mass of the silicon wafer. Better UV curing is indicated by a thinner un-polymerized layer.

To evaluate the role of each UV LED, a series of eight experiments was designed as follows: three UV LEDs were turned on, followed by turning on of two of three UV LEDs and each UV LED; lastly only the high-pressure mercury lamp was turned on.

3. Results and discussion

The thickness of the un-cured film was measured for the series of experiments and is summarized in Table 2. Hereafter, the role of each UV LED in the UV curing process is discussed.

Figure 4 shows the effect of long wavelength for compensating the low intensity of the short-wavelength UV LED emission. Experiment (2) shows the thickness of the un-polymerized layer achieved with the 365 nm and 310 nm LEDs. Experiments (5) and 7 were performed with 365 and 310 nm irradiation, respectively. The thickness of the un-polymerized layer at the end of Experiment (2) was the lowest. This result indicates that the 365 nm UV LED can be used in conjunction with the 310 nm UV LED to decrease the thickness of the un-polymerized layer.

Under irradiation with the 310 nm UV LED alone, the HCK photoinitiator was activated, whereas TPO was not well activated. When irradiation was performed with the 365 nm UV LED, TPO absorbed the light and was activated to start photopolymerization.

![Fig. 4. Effect of 365 nm UV LED for compensating the intensity of 310 nm UV LED.](image)

Figure 5 shows the results with the pair of UV LEDs and under irradiation with a single UV LED. Experiments (3) and (4) were performed with the pair of 340 and 365 nm LEDs and the 310 and 340 nm LEDs, respectively. Experiments (5), (6), and (7) involved irradiation with the 365, 340, and 310 nm LEDs alone, respectively.

The difference in the thickness of the un-polymerized layer achieved in Experiments (3) and (4), in which the 340 nm UV LED was used in conjunction with 365 and 310 nm UV LED, respectively, was less than 0.5 μm. Moreover, the thickness of the un-polymerized layer with 340 nm irradiation was the highest among that of the
samples irradiated with a single LED. This indicates that concurrent use of the 340 nm UV LED with the other LEDs as a light source is less effective for decreasing the thickness of the un-polymerized layer.

Finally, the thinnest un-polymerized layers achieved with the UV LED and the high-pressure mercury lamp were compared. Experiments (2) and (8) were performed with concomitant irradiation with the 310 and 365 nm UV LEDs and with the high-pressure mercury lamp, respectively. As shown in Fig. 7, the difference in the thickness of the un-polymerized layer was 1.2 μm, where the thickness is considered comparable. Using the 310 and 365 nm UV LEDs, the spectrum and effect of the high-pressure mercury lamp could be simulated.

The thickness of the un-polymerized layer achieved with the high-pressure mercury lamp was lower than that with the UV LEDs. This is attributed to the 405 nm emission of the high-pressure mercury lamp. TPO is sensitive to 405 nm light. The energy of the 405 nm line is less than that of the 365 and 310 nm emissions. However, TPO could dissociate, produce radicals, and start polymerization.

**4. Conclusion**

This study demonstrated the development of a hybrid UV LED device that combines different wavelength UV LEDs into one UV light source. The combination of 365 nm and 310 nm UV LEDs resulted in the thinnest un-polymerized layer among the various combinations of UV LEDs. The result was comparable to that achieved with the high-pressure mercury lamp. The thickness of the un-polymerized layer obtained with the high-pressure mercury lamp was less than that with any combination of the UV LEDs. This indicates that the 405 nm emission of the high-pressure mercury lamp functions to photopolymerize the monomer and is indispensable for the UV curing process.

Increasing the intensity of the short-wavelength
emission of UV LEDs is still a challenge because of the attendant increase in the heat loss. Removal of the heat from UV LEDs increases the footprint of the light source and the electric power required for cooling.

The results of this study were not difficult to predict on the basis of photochemistry. However, UV LED companies develop single-wavelength UV LED light sources that are not suitable for curing the formulation of resins optimized for treatment with conventional high-pressure UV lamps. The formulation is determined to meet the specifications of the final product, and it is not easy to change this formulation. Commercial UV LED manufacturers should simulate the spectrum of the high-pressure mercury lamp by optimizing the location and intensity of UV LEDs of different wavelengths in order to replace the hazardous mercury lamps with environmentally benign UV LEDs.

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