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Brief Report

Light-curing of dental resins with GaN violet laser diode:

The effect of photoinitiator on mechanical strength

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Abstract The purpose of this study was to evaluate whether a Gallium Nitride (GaN) -based violet laser diode (VLM500) could be used as a light source for light-cured dental resins. Three experimental unfilled resins containing different photoinitiators (camphorquinone, CQ; phenyl propanedione, PPD; or mono acylphosphineoxide, MAPO) were evaluated. These resins were light-cured with a VLM500 laser diode, and their ultimate micro-tensile strengths (µTS) were compared to those cured with three different LED light sources (Curenos, G-Light Prima-normal mode and G-Light Prima-PL mode). The VLM500 produced high µTS values in all three resins, and we concluded that this violet laser diode can be used as a light source for light-cured dental resin materials.

Introduction

The camphorquinone (CQ)/amine photopolymerization system is the most widely used system for visible-light cured dental restorative materials and their adhesives. To polymerize these materials, quartz-tungsten-halogen (QTH) light curing units (LCUs) are most commonly used. However, since the invention of blue light emitting diodes (blue LEDs) in the early 1990s [1], these diodes have become increasingly popular for use in light-curing units.

Recently, some manufacturers have introduced other photoinitiators such as phenyl-propanedione (PPD) and acylphosphine oxide alongside the traditional CQ/amine system. These initiators help reduce the intensity of the yellow tint and improve the photopolymerization efficiency [2, 3]. The optimal absorbance wavelengths are mostly distributed from the ultraviolet (UV) to violet visible light region; hence, photopolymerization is barely initiated by standard QTH-LCUs, and might not be initiated at all by blue LED-LCUs [4]. To overcome this problem, dual-wavelength LED-LCUs have recently been developed that combine both blue and violet LEDs [5, 6].

In 1996, Nakamura et al. developed gallium nitride (GaN) violet-laser diodes [7], which now find widespread use as light sources for high-speed and multilayer recording systems such as Blu-ray Disc and HD-DVD systems [8].

These violet-laser diodes also show promise for medical applications, such as cutting soft tissue [9], laser acupuncture [10], tooth whitening [11-14], antimicrobial photodynamic therapy [15], and the detection of dental caries [16]. It is also speculated that the wavelength of violet laser diodes is suitable for curing these alternative dental material initiators [4-6, 17, 18].

The purpose of this study is to evaluate the effect of violet laser diode curing on three unfilled experimental resins by comparing the ultimate micro-tensile strength (µTS) produced from the violet laser diode with two different commercial LED light curing units. The null hypothesis tested in this study is that the use of a violet laser diode does not enhance the mechanical strength of the unfilled resins.

Materials and Methods

Curing light sources

A GaN-based violet laser diode (VLM) was used. For comparison, two LED light-curing units were also used: CNS, which is a high-power blue LED-LCU, and GLP, which is a high-power LCU combining both blue and violet LEDs (Table 1).

The VLM light was delivered through an optical fiber with a core diameter of 800 μm. The sample was set at a distance of 16 mm from the fiber tip to obtain an irradiated area of 8 mm in diameter [15]. The stimulated emission peak of this laser was at 409 nm, with a full width at half-maximum of 7 nm (emission range: 402-416 nm). For both the CNS and GLP, a tapered light probe of 8 mm in diameter was attached to the light sources. Two different modes were used with GLP: normal mode (GLP-N) and PL mode (GLP-PL). GLP-N utilizes a combination of two different types of LEDs which are predominantly blue, with a violet LED as a minor component (three blue LEDs and one violet LED). GLP-PL mode emits only the weak violet light (1 violet LED).

Experimental resins and their spectral characterization

Three experimental unfilled resins with different photoinitiators were used: camphorquinone (CQ), 1-phenyl-1,2-propanedione, (PPD), and 2,4,6-trimethylbenzoyl diphenylphosphine oxide (MAPO) (Table 2). The concentration of photoinitiator in each resin was set at 1 wt %. A deuterium tungsten halogen light source (DH-2000, Ocean Optics, Dunedin, FL, USA) was connected to a UV-vis-NIR spectrometer (USB4000, Ocean Optics) by two optical fibers separated by a sample holder. One drop of the unfilled resin was placed onto a thin glass plate (thickness: 0.15 mm; Matsunami Glass Ind., Ltd., Kishiwada, Osaka, Japan), covered with another glass plate, and gently compressed using finger pressure. Immediately afterwards, each resin sample was placed in the sample holder and irradiated by the deuterium tungsten halogen light (DH-2000). The light transmission spectra through each adhesive sample were acquired in 0.2-nm increments.

Ultimate micro-tensile strength (μTS)

An acrylic frame of 9.0 mm in inner diameter and 0.6 mm in height was placed on a glass slide, filled with the unfilled resins and pressed using another 1-mm-thick glass slide, before being light-cured through this glass slide for 60 s. The cured resin disc was then carefully removed from the acrylic frame and immersed in 37 $^\circ$C tap water for 24 h in the dark.

After the water immersion, the resin samples were trimmed into an hourglass shape to a width of 1.2 mm at the narrowest part, by using a super-fine cylindrical diamond bur (Diamond Point SF 114, Shofu, Kyoto, Japan)

connected to 1:5 ratio high-speed motor handpiece (Ti-Max X95L, Nakanishi Inc., Kanuma, Tochigi, Japan). A continuous water spray was used during cutting. The width and thickness of the narrowest region were measured with a digital caliper (Mitutoyo, Tokyo, Japan) to the nearest 0.001 mm. The samples were then attached to a Bencor Multi-T device (Danville Engineering, San Ramon, CA, USA) using cyanoacrylate glue (Model Repair II Blue, Dentsply-Sankin, Ohtawara, Japan) and the ultimate micro-tensile strength (μTS) was measured on a universal testing machine (Tensilon RTC-1150-TSD, Orientec, Tokyo, Japan) with a cross-head speed of 1.0 mm/min [18].

The μTS, expressed in MPa, was calculated by dividing the applied force (N) by the product of width and thickness of the narrowest region (mm).

Ten specimens were used for each set of tests, and the data were analyzed using two-way ANOVA at a 5% significance level with IBM SPSS 18 statistical software (SPSS Inc., Chicago, IL, USA).

Results and Discussion

Spectrometric analyses

Figure 1 shows the light transmission spectrum from each resin. The drop in transmittance is equivalent to light absorbance. For Exp-CQ, a slight dip in the spectra was seen in the range of 430-490 nm, with an inverse peak (λ_{max}) at 472 nm. The reductions of transmittance were 3.9% at 463 nm and 1.9% at 405 nm. For Exp-PPD, the transmittance gently increased between 360-485 nm, and the reductions of transmittance were 1.9% at 463 nm and 5.9% at 405 nm, respectively. For Exp-MAPO, three inverse peaks were found at 366 nm, 381 nm, and 396 nm. The reductions of transmittance were 0.1% at 463 nm and 7.0% at 405 nm, respectively. Therefore, these results indicate that Exp-CQ might be more reactive toward blue LEDs than Exp-PPD or Exp-MAPO. Conversely, Exp-MAPO might be more reactive to violet LEDs and violet laser diodes, but it might be less reactive to blue LEDs.

µTS

µTS testing is considered to be one of the most reliable methods to determine the mechanical strength of dental adhesives because there is a statistical correlation between µTS and micro-tensile bond strength (µTBS) [19, 20]. Hence, this technique has recently found wide use in determining the influence of water/solvent content on adhesives, and long-term water storage [20-22].

8

Figure 2 shows the results of µTS testing of the resins produced by each of the four different light sources. Two-way ANOVA revealed a significant interaction between the pair of means for the factors 'photoinitiator' ($F=9.957$, $p<0.0001$) and 'curing light source' ($F=11.181$, $p<0.0001$). Furthermore, a significant interaction between these two factors was found ($F=7.757$, $p<0.0001$). Therefore, further analysis was performed using the Tukey HSD test at a significance level of $p=0.05$.

The mean µTS of Exp-CQ was greater than 100 MPa when cured with either CNS or GLP-N, with no statistically significant difference between the two results ($p=1.000$). As shown in the spectrometric analyses, the emission spectra of these two sources have maxima at wavelengths similar to the maximum absorption peak of Exp-CQ (Fig. 2). A longer curing time (60 s) and high power densities (>1000 mW/cm^2) might also be sufficient to polymerize Exp-CQ.

Similarly, no significant difference was found between the µTS of Exp-CQ and Exp-PPD cured with either CNS or GLP-N ($p=0.746$ and $p=1.000$, respectively). However, the Exp-PPD cured with CNS appears to have a slightly lower mean µTS value than CQ cured with CNS. This suggests that the photopolymerization efficiency of PPD was slightly lower than that of CQ when exited by a blue LED, which also confirms the results of spectrometric analyses.

For both Exp-CQ and Exp-PPD, the µTS when cured with GLP-PL was significantly lower than that produced by GLP-N ($p=0.004$ and $p=0.004$, respectively). The light emitted from GLP-N was produced from three blue LEDs and one violet LED; however, despite coming from the same device, the light from the GLP-PL removed the contribution of the three blue LEDs. Therefore, this difference in results clearly shows that the weak violet LED light energy is insufficient to polymerize PPD.

Under CNS light, the Exp-MAPO resin produced a significantly lower µTS value than both Exp-CQ and Exp-PPD ($p<0.001$ and $p=0.012$, respectively). The photopolymerization efficiency of MAPO has been reported to be only 1/4 of the efficiency of CQ, and 1/4.7 of the efficiency of PPD when excited by a blue LED light source [4]. This result suggests that the low value obtained in our experiments was due to insufficient polymerization.

The energy density of the GLP-PL light source was approximately 1/30 of the CNS energy density (Table 1). However, the Exp-MAPO resin cured with GLP-PL showed significantly higher µTS than when cured with CNS ($p<0.001$). It has been reported that the quantum yield in MAPO at 405 nm was 12 times of that of CQ at 470 nm [23]. Hence, our results show that MAPO can be photoactivated even by low energy density violet light sources.

The Exp-CQ resin showed significantly lower μTS when cured with GLP-PL compared to the other three light-curing sources ($p<0.05$). Chen et al. reported that the absorption coefficient of CQ at 410 nm was 1/5.4 of that at 470 nm [24]; thus, the lower mechanical strength might be caused by the insufficient polymerization at this wavelength. However, Exp-CQ cured with VLM resulted in a similarly high μTS as that produced by both CNS and GLP-N ($p=1.000$). Therefore, the lower absorption coefficient of CQ for violet light can be compensated by increasing the power density.

An unexpected result was that no significant difference was found between Exp-MAPO cured with GLP-PL and that cured with VLM ($p=0.999$). This might be due to the formation of shorter polymer chains caused by rapid polymerization kinetics under the higher energy supply from VLM. In clinical practice, if too much energy is applied to the resin, this also causes an overly rapid increase of polymerization, and thus generates shrinkage stress at the adhesive interface [25], which often results in a reduced adhesive interfacial area and secondary effects such as microleakage and white-line margin. Furthermore, heat generation may cause harm to the dental pulp. Future research should focus on the optimal conditions, for example, the power density, irradiation time and concentration of the photopolymerization initiator.

This study indicates the effectiveness of violet light for the photopolymerization of dental materials. However, as this laser device is

heavier and larger compared to LED light-curing units, it is somewhat

impractical. Downsizing the unit is desirable for daily use in a dental practice.

Conclusions

This study shows that violet laser diodes were not only effective as light sources for curing two alternative dental photoinitiators, PPD and MAPO, but also for curing the conventional initiator CQ. Therefore, the null hypothesis, which states that the use of violet laser diodes does not enhance the mechanical strength of the unfilled experimental resins, can be rejected.

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Table 1   Light sources used in this study

Code*	λ_{max} (nm)	Power density (mW/cm^2)	Time (s)	Diameter (mm)	Total energy (J)
CNS	463	1550	60	8	185.1
GLP-N	403, 463	1150	60	8	137.3
GLP-PL	403	52	60	8	6.2
VLM	409	1350	60	8	161.2

*CNS: Curenos (Shofu, Kyoto, Japan),

  GLP-N: G-Light Prima (normal mode)(GC, Tokyo, Japan),

  GLP-PL: G-Light Prima (PL mode) (GC),

  VLM: VLM 500 (Sumitomo Electronic Industries, Yokohama, Japan)

Table 2   Unfilled resins used in this study

Unfilled resin	Component
Exp-CQ	Bis-GMA (55.8%), TEGDMA (39.2%), DABE (1%), CQ (1%)
Exp-PPD	Bis-GMA (55.8%), TEGDMA (39.2%), DABE (1%), PPD (1%)
Exp-MAPO	Bis-GMA (55.8%), TEGDMA (39.2%), DABE (1%), MAPO (1%)

Bis-GMA: bisphenol A diglycidylmethacrylate,

TEGDMA: triethylene glycol dimethacrylate,

DABE: *N,N*-dimethyl-p-amino benzoic acid ethyl ester,

CQ: camphorquinone,

PPD: 1-phenyl 1,2-propanedione,

MAPO: 2,4,6-trimethyl benzoil diphenyl phosphine oxide

Figure Legends

Figure 1 Transmittance spectra of the experimental resins used in this study

Figure 2 Ultimate micro-tensile strength grouped by light source (Mean (S.D.),

MPa; n=10). Results with the same letter represents no statistically
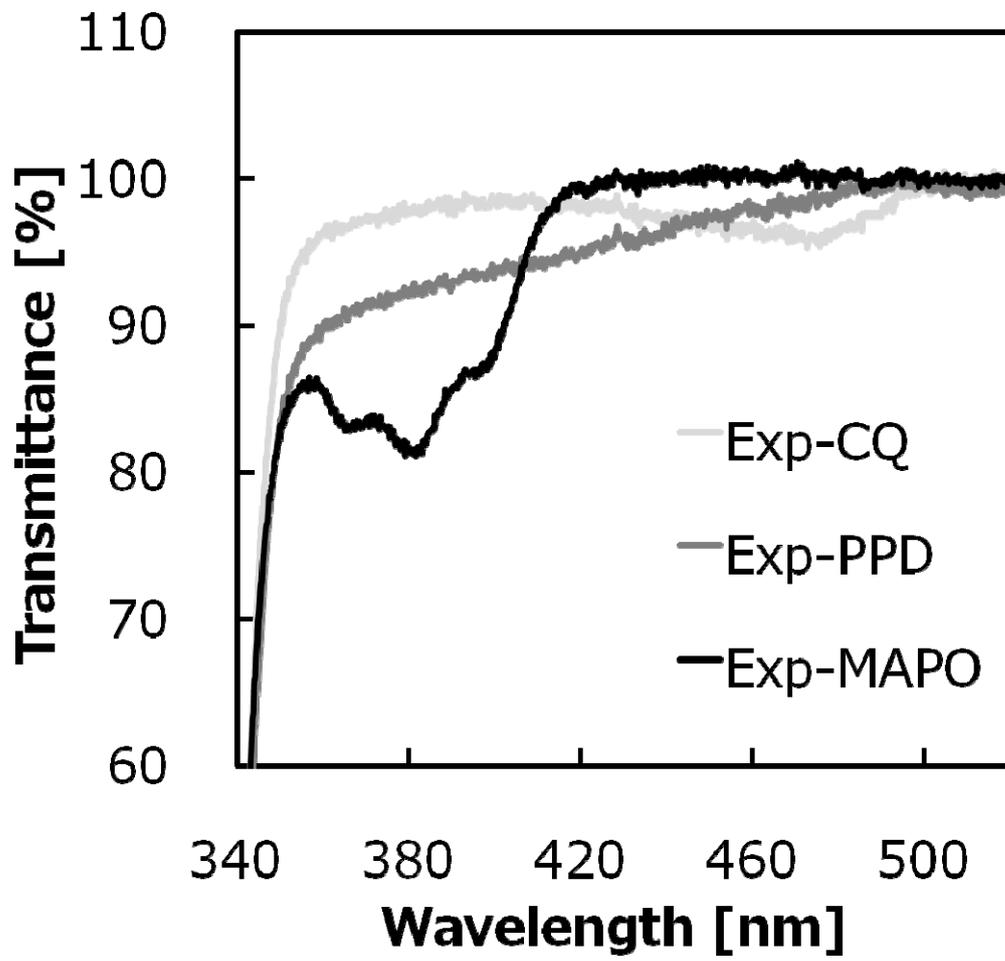
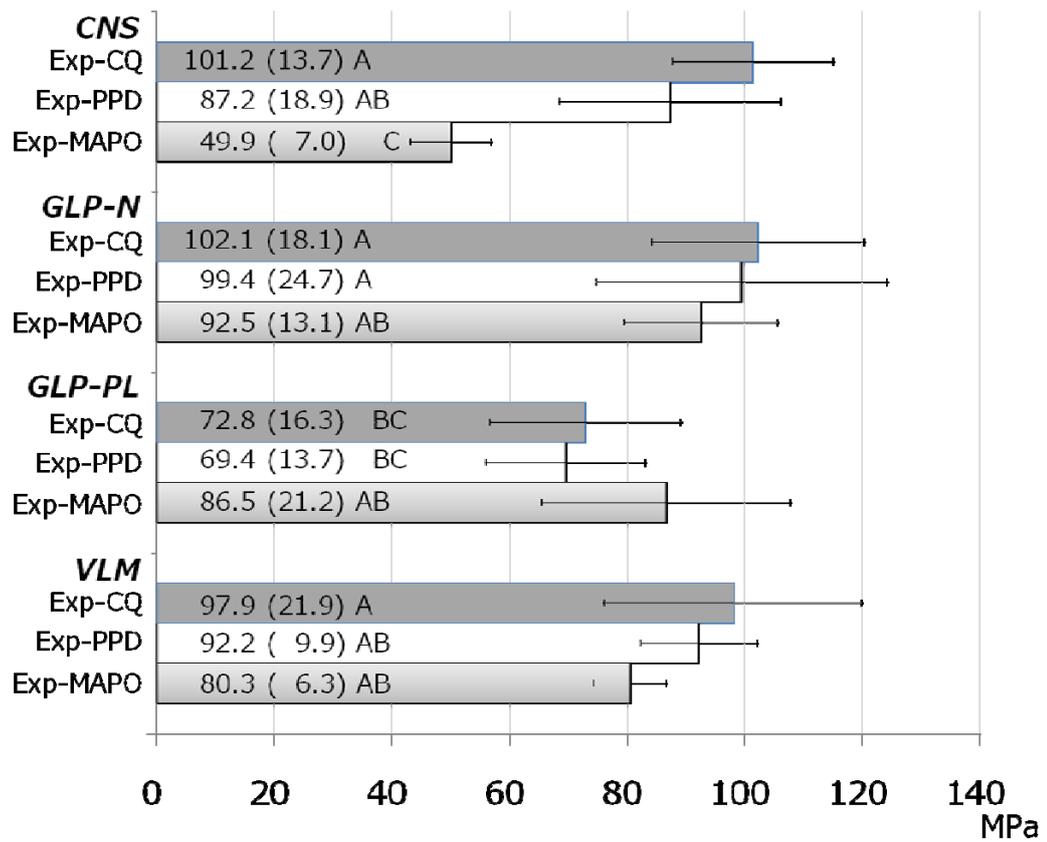significant difference (Tukey HSD test; $p>0.05$).

Figure 1

CNS
- Exp-CQ: 101.2 (13.7) A
- Exp-PPD: 87.2 (18.9) AB
- Exp-MAPO: 49.9 (7.0) C

GLP-N
- Exp-CQ: 102.1 (18.1) A
- Exp-PPD: 99.4 (24.7) A
- Exp-MAPO: 92.5 (13.1) AB

GLP-PL
- Exp-CQ: 72.8 (16.3) BC
- Exp-PPD: 69.4 (13.7) BC
- Exp-MAPO: 86.5 (21.2) AB

VLM
- Exp-CQ: 97.9 (21.9) A
- Exp-PPD: 92.2 (9.9) AB
- Exp-MAPO: 80.3 (6.3) AB

0   20   40   60   80   100   120   140   MPa

Figure 2