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빛의 파장이 복합레진의 경도와 중합수축에 미치는 영향

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Effects of light wavelength on the microhardenss and polymerization shrinkage of composite resins

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광 개시를 위하여 광원(파장)의 선택은 중합의 결과에 영향을 미친다. 본 연구는 광원의 파장이 복합레진의 중합에 미치는 영향을 평가한 것이다. 이를 위하여 4가지의 광조사 유닛과 3종의 복합레진을 사용하였고 광 조사된 시료는 미세경도와 중합수축을 평가하였다. 그 결과 광 개시제로 camphorquinone과 coinitiator를 함유한 레진은 473 nm의 파장을 가지는 레이저에 의해 시료 표면의 미소경도가 405이나 457 nm 파장의 레이저 때보다 다소 낮았다. 405 nm 레이저의 경우는 camphorquinone만 함유한 레진에서 가장 낮은 미소경도를 보였다. 시료의 바닥면에서는 광원의 파장이 405에서 473 nm로 증가할수록 미소경도도 증가하였다. 중합수축의 경우 LED를 광원으로 한 경우가 가장 큰 수축값을 보였다. 이를 통해본 연구는 파란색의 레이저가 LED 광원처럼 다양한 복합레진을 중합할 수 있는 가능성을 제시하였다.

색인단어 : 복합레진; 빛의 파장; 미세경도; 중합수축

INTRODUCTION

Light-curing composite resins initiate their free radical-mediated polymerization by activating the photoinitiator, camphorquinone (CQ), with the aid of an externally irradiated blue light. The CQ excited optically by an external light then receives a proton from an amine accelerator, such as DMAEMA (N,N-dimethylaminoethyl methacrylate), and these two become free radicals by taking and losing a proton, respectively. The radicals formed combine with the monomers to be stabilized and then a chain-reaction occurs until the reaction terminates. Therefore, a photoinitiator is essential to initiate the process. Generally, CQ less than 1 wt.% is added to the composite resins as a principal initiator. CQ is a yellow powder that absorbs blue light at approximately 380-500 nm. Recently, some composite resins contained a coinitiator by lowering the CQ content to overcome the CQ-related color instability issue [Santini et al., 2012; Schneider et al., 2008; Park et al., 1999]. Because monomer to polymer conversion in composite resins during the polymerization process is maximum 70%, the residual monomers and CQ cause color instability due to oxidation and the inherent yellow color [Brackett et al., 2007; Sideridou et al., 2003]. Most coinitiators have their light absorption band in the UV region, even though some coinitiators extends to the visible

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region [Leprince et al., 2011; Price and Felix, 2009;].

As a light source, the photon supplier, the conventional quartz-tungsten-halogen based light-curing units (LCUs) have emission bands that cover the entire and some portion of the CQ and coinitiator absorption bands [Dogan et al., 2009; Asmussen & Peutzfeldt, 2005]. On the other hand, the popularity has recently shifted to light-emitting diode (LED) LCUs. Based on the development of LED technology, LED LCU can emit high intensity light with portability and an extended lifetime [Marchan et al., 2011; Leprince et al., 2010; 고 등, 2005. LED LCU emits light near the absorption peak of CQ with a much narrower band width than QTH LCUs.

Compared to QTH and LED LCUs, lasers have exceptional features as a light source. A laser has an extremely narrow emission band width and coherent nature, so almost all the photons emitted from the laser device have the same wavelength and phase. Among the lasers, the argon laser has been used as a LCU for curing composite resins because one of the argon emission wavelengths (488 nm) matches the CQ absorption band at its tail part [Cassoni et al., 2010; Tielemans et al., 2009]. However, owing to its bulky size and high cost, acceptance in the clinics was limited. In addition to the argon laser, diode-pumped solid state (DPSS) lasers and diode lasers of various wavelengths that match either of the CQ or coinitiator emission bands have recently become available [Park et al., 2016; Baek et al., 2013; Kapoor et al., 2008; Habbersett et al., 2007]. Therefore, assessing these lasers for the curing of composite resins will help better understand the effects of wavelength on the polymerization of various composite resins. The aim of the present study was to test how the wavelength of the light sources affects the degree of polymerization of composite resins, which contain CQ only or CQ+coinitiator as a photoinitiator, by evaluating their microhardness and polymerization shrinkage.

MATERIALS AND METHODS

1. Specimens and light-curing conditions

For this study, three different composite resins [Aelite LS Posterior (AES), Tetric EvoCeram (TEC), Filtek Z350XT (FZ3)] were used (Table 1 shows compositional details). All have the same shade, A3. For light curing, three

Table 1. Materials used in the present study

Code	Composition	Filler content vol%/wt%1/wt%2	Manufacturer
AES	Bis-EMA, TEGDMA, glass frit, amorphous silica,	74/ 88/ 85.8	Bisco, Schaumburg, IL, USA
TEC	Bis-GMA, UDMA, Ba-Al-Borosilicate filler, $Al2O_3$,YbF_3	57/ 80.5/ 73.0	Ivoclar Vivadent, Schaan, Liechtenstein
FZ3	Bis-GMA, UDMA, TEGDMA, Bis-EMA, zirconia/silica	63.3/ 78.5/ 74.7	3M ESPE, St Paul, MN, USA

AES: Aelite LS; TEC: Tetric EvoCeram; FZ3: Filtek Z350XT
Bis-EMA: ethoxylated bisphenol A glycidyl methacrylate; Bis-GMA: bisphenol A glycidyl methacrylate; TEGDMA: triethyleneglycol dimethacrylate; UDMA: urethane dimethacrylate
wt%[1]: nominal weight (according to the information supplied by the manufacturers)
wt%[2]: weight by ash method

different lasers, 405, 457, and 473 nm (LVI Technology, Seoul, Korea), and one LED light-curing unit (LCU) [L.E.Demetron (LED), Kerr, Danbury, CT, USA] were used. Fig. 1 shows the emission spectra of the lasers and the absorption spectrum of the photoinitiator (camphorquinone, CQ), which is commonly contained in composite resins. Among the specimens, AES and TEC contain a coinitiator in addition to CQ, even though the manufacturers did not specify the precise name of the coinitiator. The probable coinitiators, PPD (1-phenyl-1,2-propanedione) and Lucirin TPO [diphenyl (2,4,6-trimethybenzoly) phosphinoxid], based on recent other studies, were also added in Fig. 1. The output light intensity of LED was approximately 900 mW/cm^2, as measured using a built-in radiometer, and the output power and spot size of the lasers beam were approximately 150 mW (PM3/FIELDMAX, Coherent, Portland, OR, USA) and 6 mm, respectively. The resulting light intensities were approximately 530 mW/cm^2.

2. Microhardness test

To measure the surface microhardness (Hv) of the specimens, the resin was filled into a metal mold (4×2×3 mm) and light cured for 40 s using four different LCUs. Light irradiation was performed only through the top surface of the specimen. The cured specimens were then removed from the mold and aged for 24 h at 37℃ in a dry, dark chamber. The microhardness of the top (z=0) and bottom (z=3 mm) surfaces were measured using a Vickers hardness tester (MVK-H1, Akashi, Tokyo, Japan) by evaluating the size of the microindentations (n=12 for each test

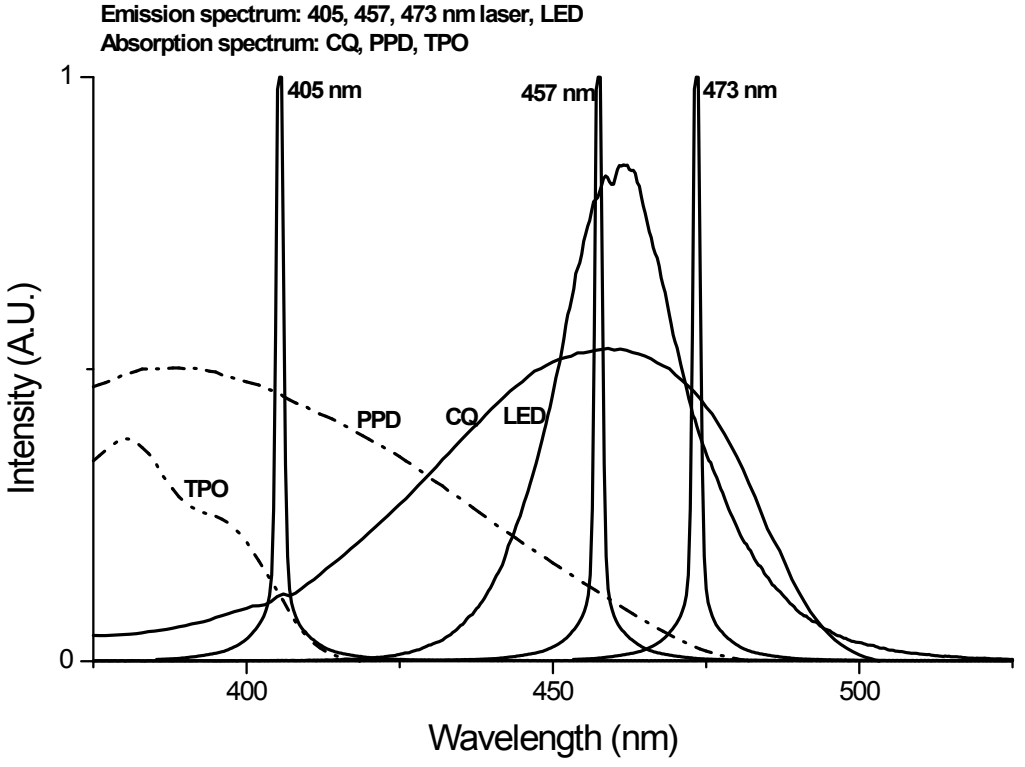

Figure 1. Emission spectrum of the tested LCUs (405, 457, 473 nm laser, and LED unit) and absorption spectrum of photoinitiators (CQ, PPD, and TPO).

condition) made using a 200 gf load and a 10 s dwell time.

3. Polymerization shrinkage measurement

The polymerization shrinkage (μm) that occurred during and after light curing were measured (n=7 for each product) using a linometer (RB 404, R & B Inc., Daejeon, Korea). A cylindrical shape resin (diameter: 4 mm, thickness: 2 mm) was placed over an aluminum disc (the specimen stage of the measurement system) and its top surface was covered with a glass slide. The end of the light guide (LED) was then placed in contact with the glass slide (in the case of the laser, the guided light using a reflecting mirror was irradiated over the specimen vertically). Before light curing, the initial position of the aluminum disc was set to zero. Light was irradiated for 40 s. As polymerization progressed, the specimens shrank away to the light source and the aluminum disc under the resin moved to the light source. The level of disc displacement, which is a measure of polymerization shrinkage, was measured automatically for 130 s using a non-contacting inductive sensor placed below the aluminum disc. The resolution and measurement range of the shrinkage sensor were 0.1 μm and 100 μm, respectively.

4. Statistical analysis

The microhardness and polymerization shrinkage results were analyzed using two-way ANOVA followed by a post-hoc Tukey test for multiple comparisons. Statistical significance was accepted for $p<0.05$.

RESULT

Table 2 shows the microhardness of the specimens obtained using the different LCUs. On the top surfaces, the microhardness of the specimens ranged from 40.1 to 85.6 Hv depending on the resin product and LCU. Overall, the microhardness values obtained were significantly different ($p<0.001$), but the results from the 405 and 457 nm lasers were similar. Among the cases, AES and TEC (coinitiator-containing), which were cured using the 473 nm laser, showed the lowest microhardness. On the other hand, FZ3 (only CQ-containing) showed the highest and lowest microhardness when cured using the LED and 405 nm laser, respectively.

On the bottom surface, the microhardness of the specimens ranged from ND (not detectable) to 75.1 Hv

Table 2. Microhardness of the specimens in their top and bottom surfaces

	Top surface				Bottom surface		
	AES[1]	TEC[2]	FZ3[3]		AES[1]	TEC[2]	FZ3[3]
405 nm[a]	80.4±3.6	51.3±1.6	75.7±2.6	405 nm[a]	ND	26.5±1.7	31.1±2.3
457 nm[a]	82.1±0.4	42.5±0.4	80.9±0.5	457 nm[b]	33.4±0.7	36.7±0.8	67.2±0.6
473 nm[b]	73.7±1.9	40.8±1.2	79.7±1.4	473 nm[c]	44.8±2.7	37.1±1.3	75.1±1.2
LED[c]	82.8±0.6	47.5±0.8	85.6±0.5	LED[d]	46.2±1.2	40.9±0.8	72.8±0.4
p-value	α <0.001,	β <0.001,	$\alpha \times \beta$ <0.001		α <0.001,	β <0.001,	$\alpha \times \beta$ <0.001

* ND means not detectable
* Statistically significant difference for LCU is shown by superscript lettersa,b,.., on resin product by superscript numbers1,2,.. Same letters or numbers are not significantly different (p>0.05).
* On p-values, the letters α and β denote LCU and resin product, respectively.

depending on the resin product and LCU. The surface of AES cured by the 405 nm laser was so soft that the microhardness was indeterminate. Overall, the microhardness values obtained were significantly different (p<0.001) regardless of the resin product and LCU. Among the LCUs, the 405 nm laser produced the lowest microhardness on the bottom surface followed by the 457 nm laser.

Table 3 summarizes the polymerization shrinkage of the specimens. Polymerization shrinkage ranged from 7.2 to 15.7 μm for the 2 mm-thick specimens depending on the resin product and LCU. Among the specimens, FZ3 showed significantly higher shrinkage values (10.9-15.7 μm) (p< 0.001). Among the LCU, the LED induced the greatest shrinkage (10.5-15.7 μm) regardless of the resin product.

DISCUSSION

Basically, light-curing composite resins contain CQ as a principal photoinitiator. As shown in Fig. 1, CQ can absorb blue light from 380 to 500 nm. Because CQ is a yellow powder and does not photobleach completely, its yellowness can cause color instability due to the oxidation of residuals, which raises aesthetic issues, even though the content in composite resins is limited [Brackett et al., 2007; Sideridou et al., 2003]. To handle the color issue, some composite resins contain a coinitiator, such as DMBZ (2,2-dimethoxy [1,2] diphenyletanone), PPD (1-phenyl-1,2-propanedione), and TPO [diphenyl (2,4,6-trimethybenzoly) phosphinoxid], which allow a lowering of the CQ content in their resin matrix [Santini et al., 2012; Schneider et al., 2008; Park et al., 1999]. As shown in Fig. 1, most coinitiators have their absorption spectrum in the UV region, even though PPD can absorb light at wavelengths much longer than 450 nm.

Table 3. Polymerization shrinkage of the specimens by the different LCUs

	Top surface		
	AES[1]	TEC[1]	FZ3[2]
405 nm[a]	7.2 ± 0.6	9.9 ± 0.6	10.9 ± 1.0
457 nm[b]	10.4 ± 1.2	8.5 ± 1.0	12.2 ± 0.5
473 nm[c]	11.3 ± 0.6	9.3 ± 0.5	13.1 ± 1.2
LED[d]	11.4 ± 0.5	10.5 ± 0.1	15.7 ± 0.5
p-value	α <0.001,	β <0.001,	$\alpha \times \beta$ <0.001

The wavelengths of the LCUs tested in the present study matched CQ and/or the potential coinititator. The light from the 405 nm laser can be absorbed in CQ and TPO with low absorbance. On the other hand, the light can be absorbed maximally in PPD because PPD shows its absorption peak near 395 nm. The light from 457 nm can be absorbed maximally and weakly in CQ and only in PPD, respectively. In case of 473 nm, it can be absorbed maximally in CQ and negligibly low in PPD. The LED tested emitted light from 425 to 525 nm. Therefore, LED can be absorbed in PPD and CQ. Owing to the wide emission range, among the LCUs tested, the LED matched most closely with CQ. The LCUs tested have much different light intensities. The highest intensity of the lasers is approximately 59% that of a LED. A low intensity suggests fewer photons if the spot size and wavelength are fixed. Because the laser has a highly monochromatic nature (extremely narrow emission bandwidth), all the photons in each laser have a similar wavelength. On the other hand, LEDs have photons with much different energies (wavelengths). Through an evaluation of the degree of polymerization, better conditions for light curing between narrow but highly monochromatic light and wide but high light intensity light can be revealed.

The microhardness test is a useful method for evaluating the degree of polymerization determined by measuring the

size of microindentation on the surface of a specimen made by the loaded microindenter [Kim et al., 2016]. Basically, the microhardness depends much on the light intensity (mW/cm^2) because of photons and consequently the degree of photoinitiation [Kilinc et al., 2011; Versluis et al., 2004]. Among the specimens, AES and TEC may contain a coinititator in addition to CQ even though the precise identity has not been disclosed by the manufacturers. Higher microhardness values (80.4 and 82.1 Hv) by the 405 and 457 nm lasers than that by the 473 nm laser indicates that AES and TEC surely contain a coinitiator in addition to CQ. Among the coinitiators, AES may contain PPD because TPO has a much weaker absorbance near 405 nm than PPD. Therefore, achieving high microhardness does not appear probable with such lower absorbance. The lowest microhardness of AES and TEC by the 473 nm laser is due to the negligibly low absorbance of PPD at 473 (the same result will be possible for TPO due to no light absorption at the 473 nm region). The lowest microhardness of FZ3 for the 405 nm laser implies no containing of a coinitiator in this resin product. The highest microhardness by the LED is due basically to the much higher (1.7 times) light intensity than that of lasers. In the case of FZ3, the specimens cured using lasers have at worst, 11.6% lower microhardness than that by LED even with a 59% lower light intensity. This suggests that the 473 nm laser can polymerize ordinary CQ-based composite resins to a level close to that achieved using the LED LCU.

On the bottom surfaces, the specimens cured using the 405 nm laser showed the lowest microhardness, and as wavelength of the LCU changed from 405 to 473 nm, the microhardness gradually increased regardless of the resin product. The slightly lower microhardness by the 405 and 457 nm lasers, regardless of the resin product, than those by the LED would be due mainly to the lower light intensity. Also, as the wavelength of incident light becomes smaller than the filler sizes, the resulting light intensity decreases by $\sim 1/\lambda^4$ due to the increased scattering known as Rayleigh scattering(many of the fillers contained in the resin matrix are larger than the size of the light wavelength) [Watts & Cash, 1994].

Polymerization shrinkage is a bulk structural change that is caused by shortening of the molecular distance. Polymerization shrinkage inevitably occurs when the governing force between molecules changes from van der Waals to covalent bonds. Because covalent bond has a much stronger force than van der Waals bond, shortening of the molecular distance and the subsequent collective shortening (shrinking) of the bulk structure follows. In many cases, it produces clinically negative effects such as postoperative sensitivity, occurrence of second caries, and bond failure [Irie et al., 2002; Davidson & Feilzer, 1997]. Among the LCUs, the greatest shrinkage by the LED appears natural due to the 1.7-times higher light intensity than the lasers. Among the resin products, the highest shrinkage of FZ3, regardless of the LCU, would be due to the greater polymerization. The bottom surfaces of the two other resin products showed much lower microhardness than FZ3, even though AES and FZ3 have a similar top surface microhardness. This is due partly to incomplete polymerization, so there would be less shrinkage due to insufficient curing.

CONCLUSION

Within the limitations of the present study, the following conclusions could be reached:

1. The resin products cured using lasers with different wavelengths achieved a similar or slightly lower (〈16% at worst) microhardness, even though the light intensity of the lasers was approximately 59% of the LED LCU.
2. For the specimens (AES and TEC) containing a coinitiator, the 405 and 457 nm lasers produced a

slightly higher microhardness than that by the 473 nm laser. On the other hand, their microhardness on the bottom surface was lower than that by the 473 nm laser.

3. Specimens cured using the LED induced the greatest polymerization shrinkage compared to the other lasers. The tested lasers of different wavelengths have useful potential for the curing of composite resins with alone or in combinations.

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Effects of light wavelength on the microhardenss and polymerization shrinkage of composite resins

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As an activator of photoinitiator, the selection of a light source (wavelength) can affect the result of polymerization. This study examined how the wavelength of a light source affects the curing of composite resins. Four light-curing units (LCUs) (405, 457, and 473 nm lasers with 530 mW/cm2 and one light-emitting diode (LED) with 900 mW/cm2) and three composite resins (one only camphorquinone-containing and two camphorquinone+coinitiator-containing as an initiator) were used. To determine the degree of polymerization, the microhardness and polymerization shrinkage were assessed. On the top surface, two camphorquinone+coinitiator-containing specimens cured using the 473 nm laser showed slightly lower microhardness than those cured using the 405 and 457 nm lasers. However, specimen that contains only camphorquinone showed the lowest microhardness when cured using the 405 nm laser. On the bottom surface, the microhardness increased gradually as laser wavelength changed from 405 to 473 nm. The specimens cured using the LED LCU showed the highest polymerization shrinkage compared to that by the lasers. This study highlights the potential of blue lasers on the curing of various composite resins to the level that the LED LCU can achieve.

Key Words : Composite resin, Light wavelength, Microhardness, Polymerization shrinkage