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Clinical Relevance

Many curing lights that are present in clinical practice today cause the clinician to wonder which curing unit is best for the photopolymerization of dental light curing materials. This study introduces the blue diode laser photopolymerization of composite materials, which, if acceptable for clinical use, offers the best polymerization properties compared to other units available on the market today.

SUMMARY

Under clinical conditions, the time needed for the proper light curing of luting composites or the multi-incremental buildup of a large restoration with halogen curing units is quite extensive. Due to the development of high power curing devices, such as argon lasers and plasma arc lights and, in order to decrease curing time, halogen and LED devices have developed a high intensity polymerization mode.

This study compared the degree of conversion using Fourier Transform Infrared Spectroscopy (FT-IR) of two composite materials: Tetric Ceram and Tetric EvoCeram polymerized with three polymerization modes (high, low and soft mode) of a Bluephase 16i LED curing unit and blue diode laser intensity of 50 mW on the output of the laser beam and 35 mW/cm^2 on the resin composite sample.

Descriptive statistic, *t*-test, ANOVA, Pearson Correlation and Tukey Post hoc tests were used for statistical analyses. The results show a higher degree of conversion for the polymerization of composite samples with all photopolymerization modes of the LED curing unit. However, there is no significant difference in the degree of conversion between the LED unit and 50-second polymerization with the blue diode laser. Tetric EvoCeram shows a lower degree of conversion regardless of the polymerization mode (or light source) used.

INTRODUCTION

Light activated resin composites and curing lights for their photopolymerization have rapidly changed since first being introduced into clinical use. Although light-

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cured composites are excellent for aesthetics procedures, both the physical and chemical properties of filled resin composites are directly related to their degree of conversion. Characteristics, such as composition of composite material, brand and shade, cavity preparation geometry and composite layer thickness, light intensity and polymerization time, can modify the final properties of material. Adequate polymerization of the composite materials is fundamental for optimal physical and chemical properties and best clinical performance.[1] The depth of cure for composite materials can be affected by several factors associated with the source of light polymerization, including spectral emission (wavelength distribution), light intensity, exposure period, irradiation distance and composition of composite material. Incomplete cure of the material leads to lower mechanical properties and wear performance; leakable residual monomer and color stability may decline as well. A lower degree of conversion also leads to degradation, substance loss and fracture, therefore, the lifespan of the restoration.[2] However, if conversion is maximized to reduce the above mentioned difficulties, then alternative problems of polymerization shrinkage and brittle fracture of the composite become more critical.

Curing lights, their intensity and curing time are among the most important factors that influence the degree of conversion of composite materials. It is well known that a higher light intensity may result in a greater degree of conversion. However, high density also leads to greater polymerization shrinkage and temperature rise.[3] In recent years, many new photoactivation techniques have been proposed, such as the programmed use of low and high intensities of standard halogen curing lights, plasma lights, and lately, a new technology employing light-emitting diodes (LED).[4] Visible light curing materials generally contain a diketone-type photoinitiator that absorbs light in the 400-500 nm range and is covered with blue light from the visible spectrum. The most common photoinitiator used is camphorquinone (CQ), which has a peak absorption maximum at 468-470 nm.[5] A primary factor affecting polymerization of resin composite includes the physical composition of the material, specifically the type and concentration of photoinitiators.[6]

A quartz-tungsten halogen unit with spectral wavelength between 400-500 nm and energy output or light intensity of 300-1000 mW/cm^2 has been the source of polymerization used most frequently in contemporary dental practice.[6-7] Halogen curing lights are derived from relatively low-cost technology. However, they have low efficiency and present several drawbacks.

Plasma arc curing lights have been introduced with the claim that they can decrease curing times significantly without a concomitant reduction in mechanical properties and performance of the cured materials. Scientific data, however, does not unequivocally support this claim.[8-9]

Conventional LED units use narrow spectral emission and, because of that, have low amounts of wasted energy and minimum heat generation. Studies have shown that powerful LED units have the potential to replace conventional halogen units.[6-7]

In experimental conditions, argon and pulsed blue lasers were also tested. They have the advantage of having narrow spectral emission characteristics that may be well adapted to dental photoinitiators.[5,10-12] However, because of their construction and cost, they are not acceptable for clinical use. Laser technology has rapidly developed during last two decades. Its applications have been successfully implemented in the medical professions.[13]

This study compared degree of conversion of resin composite samples polymerized with blue diode laser and new high power LED curing units.

METHODS AND MATERIALS

For degree of conversion measurements, two composite materials were used: Tetric Ceram (Vivadent, Schaan, Liechtenstein [TC] Lot G06853, exp 2008-03) and Tetric EvoCeram (Vivadent [TEC] Lot H29941, exp 2009-10), both A2 shade (Table 1). Each composite material was polymerized with a high ([B16H] 1600 mW/cm^2, 10 seconds polymerization), low ([B16L] 650 mW/cm^2, 30 second polymerization) and soft ([B16S] 650 mW/cm^2 first five seconds, 1600 mW/cm^2 next 10 seconds of illumination) polymerization mode of Bluephase 16i LED curing unit (Vivadent) and with diode pumped solid state (DPSS) laser for 20 (DL2), 30 (DL3), 40 (DL4) and 50 (DL5) seconds (Specification—Model: VA series;

Table 1: *Composition of Composite Materials Used in This Experiment*

Composite Material	**Anorganic Filler**	**Particle Size**	**Organic Matrix**
Tetric Ceram (TC)–fine particle hybrid composite	79% w Barium glass, ytterbium trifluoride, Ba-Al-fluorosilicate glass, highly dispersed silicon dioxide, spheroid mixed oxide (79% w)	0.04-3.0 µm mean size 0.7 µm	20.2% w
Tetric EvoCeram (TEC)—nanohybrid composite	75-76% w Barium glass, ytterbium trifluoride, mixed oxide, prepolymer (82-83% w)	40 nm-3.000 nm, mean size 550 nm	17-18% w

Wavelength: 474 nm; Output power: 50 mW, light power density for polymerization of the resin composite sample was 35 mW/cm^2; Mode: TEM00; Beam roundness: >90%). The LED curing unit was new and the output light intensity was not separately measured. The absorption spectra of each tested light source is shown on Figures 1 and 2.

The diode blue laser is designed with high beam quality, energy efficiency, high reliability and ruggedness. Solid state lasers are inherently smaller, more efficient and more reliable than traditional ion lasers, as they contain no fragile gas tubes. They also have a slightly elliptical beam, where the beam can be as much as two times bigger on one axis. In the case of the laser used in this study, the beam is less than 10% bigger on one axis, making it nearly round. In all measurements, the beam was enlarged by a convergent lens to a physical spot size that is approximately 20% to 30% bigger than the prepared samples. Thus, the samples were illuminated with near uniform light. Precision electronics keep the laser temperature stabilized to maintain output power.

For the degree of conversion measurements, a total of 140 samples were prepared. For polymerization with each light illumination program, 10 samples were prepared for each illumination mode for both TC and TEC, totaling 70 samples for each material. The samples polymerized with the low polymerization mode of the Bluephase 16i curing unit served as the control group.

For the composite samples, a small amount—40 mg of unpolymerized composite material—was weighed on a Mettler Type PM 200 weighing machine (Mettler Instrumente AG, Greifensee, Zurich, Switzerland). This amount of composite material was then placed on one celluloid Mylar foil (2x2 cm size) and covered with another Mylar foil of the same size. The prepared sample was put on one round inox plate (diameter 2 cm) and covered with another inox plate of the same size. The inox plates were used to keep the sample in the same position. The two inox plates, with the resin composite sample between them, were pressed into a standard hand press at 10^7 Pa pressure to a 0.1 mm thickness. The inox plates were removed and the blue light source was placed on the upper Mylar foil of the unpolymerized sample and polymerized.

The degree of conversion of the composites used in this study was measured using an FT-IR spectrometer (Perkin-Elmer, model 2000, Beaconsfield, Buckinghamshire, UK) operating in transmittance mode immediately after using a curing device to polymerize the resin sample. The FT-IR spectra were taken at room temperature in the IR range 4000-400 cm^{-1}, with resolution 4 cm^{-1} and 20 scans per sample. The cured samples were recorded in the form of thin films.

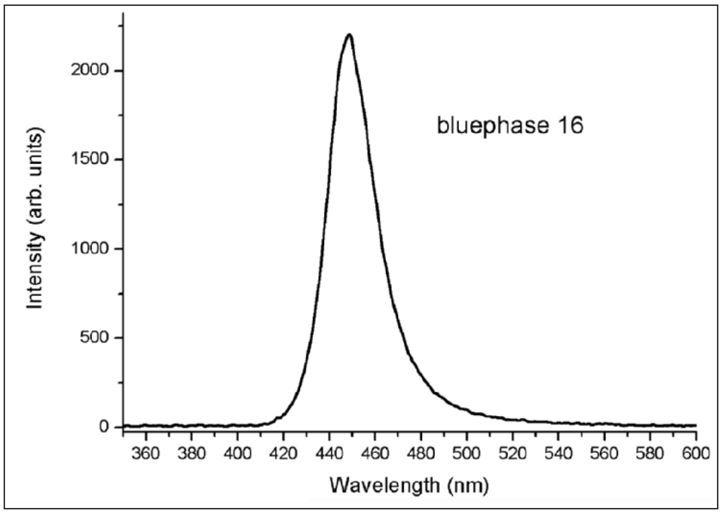

Figure 1: *Absorption spectra of the Bluephase 16i LED curing unit.*

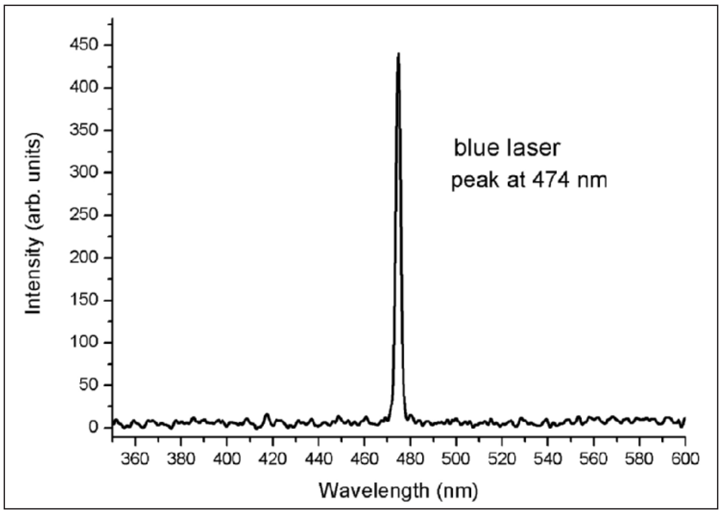

Figure 2: *Absorption spectra of the diode blue laser.*

Approximately 2 mg of uncured samples were diluted in ~100 mg of spectroscopically pure KBr matrix in agate mortar, then pressed into small discs using a standard press with 5 t/cm^2 of pressure. The IRDM (IR Data Manager) program, which was supplied by the FT-IR spectrometer manufacturer, was used to process the obtained spectra. The spectra were converted into absorbance mode, then the degree of conversion was determined using the standard method described by Rueggeberg and others.[14] This method accounts for the change in aliphatic carbon-to-carbon (C=C) double bond absorbance at 1636 cm^{-1} related to the aromatic C=C absorption peak at 1608 cm^{-1} as the internal standard. The ratio of the peaks area of the cured and uncured samples was used to calculate the degree of conversion according to the following formula:

% conversion = (1 - P/N) x 100, where P = cured and N = uncured sample.

Descriptive statistic, *t*-test, ANOVA, Pearson Correlation and Tukey Post hoc tests were used for statistical analyses.

RESULTS

Results of the one-way ANOVA test exhibited a significant difference in the setting of both composites, depending on the various light sources or polymerization modes and length of illumination in the case of the blue diode laser ($p<0.001$).

The Tukey post hoc test clarified that, in the case of the TC composite material, there is no significant difference in the illumination combinations DL4 and DL5 and DL4 and B16L of the LED of the B16H and B16S modes curing unit Bluephase 16i. All other combinations showed a significant difference. Regarding light intensity of the polymerization mode in TC composite, there was no statistically significant difference between illumination with DL3 and DL4, DL5 and B16H polymerization mode and among all modes of the Bluephase 16i LED light source, while other combinations showed a significant difference.

Pearson correlation points to a positive linear correlation between the choice of light source and the setting of each composite material ($p<0.001$).

The greatest degree of conversion was achieved for TC composite material in the case of polymerization with the B16H (67.72%) and B16S (67.86%) modes and for TEC, in the case of polymerization with the B16S (60.73%) polymerization mode. TEC exhibited a lower degree of conversion compared to TC composite material for all tested light sources (polymerization modes) (Figure 3).

In general, analysis of the results showed a significant difference in the degree of conversion of TC and TEC composite material, depending on the light source and better setting of the material with the Bluephase 16i LED curing unit compared to the blue diode laser.

The absorption spectra of TC and TEC are shown on Figures 4 and 5.

DISCUSSION

Standard halogen curing units produce white light, which must be filtered to emit only the blue spectrum of visible light. To generate blue light, the lamps must be heated to very high temperatures, resulting in the emission of heat through the curing light tip.[15] This heat transmission to the material may be responsible for the higher depth of cure, because heat increases mobility of the monomers, thus increasing the probability of the occurrence of conversion.[16]

LED combines two different semiconductors (p-n junctions). When voltage is applied, the electrons and holes recombine at the LED's p-n junctions, leading to emission of blue light. The spectral output of gallium nitride blue LED falls conveniently within the absorp-

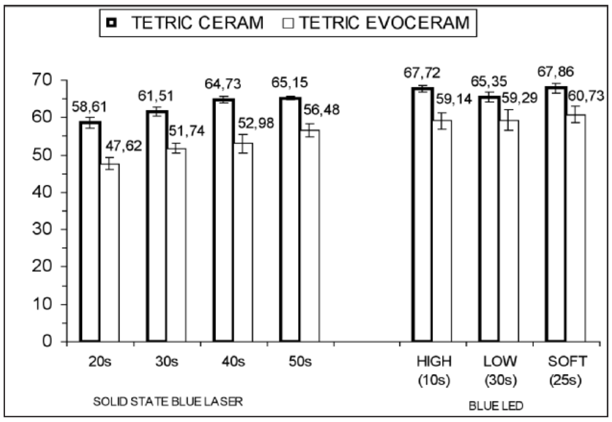

Figure 3: *Results of the degree of conversion for TC and TEC in the case of polymerization with LED curing unit Bluephase 16i and diode blue laser.*

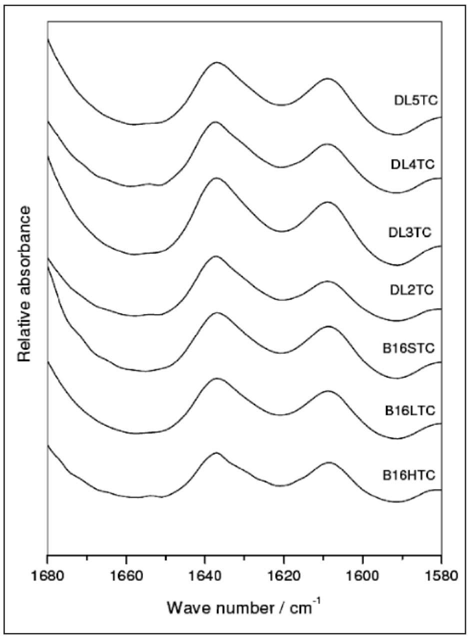

Figure 4: *Polymerization spectra of TC composite material polymerized with different curing modes.*

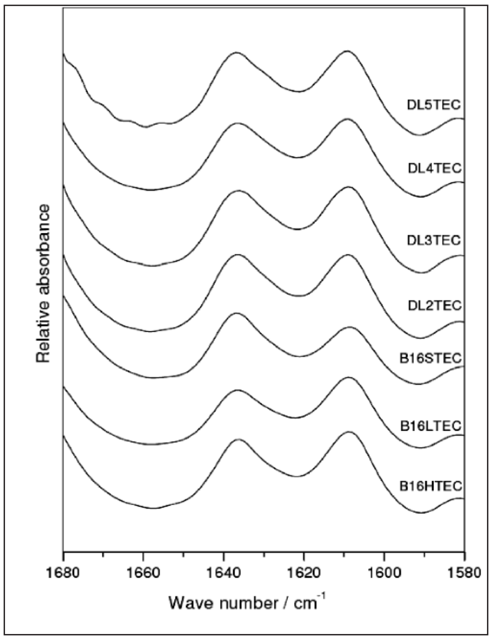

Figure 5: *Polymerization spectra of TEC composite material polymerized with different curing modes.*

tion spectrum of camphorquinone, thus, no filters are required in LED light curing units.[17-18]

The laser's beam implies stimulated emission of radiation and differs from the conventional light source. It is a single wavelength (monochromatic), collimated (very low divergence), coherent (photons in phase) and intense.[13] Since the early 1980s, one research focus has been to use the argon laser for photopolymerization of resin composite restorative materials.[19] This interest has arisen because the wavelength (488 nm) of light emitted by the argon laser is optimal for the initiation of polymerization of resin composites. The parameters of conventional halogen units are not uniform during their lifetime. Bulbs, reflectors and light tips degrade and filters become baked from heat generated by the units, which leads to a slowly altered spectrum of light. Because of the properties of the argon laser, resin composite polymerization is greater with this laser than when standard curing units are used. However, there is also a higher temperature rise and polymerization shrinkage.[19]

A pulsed laser may be a solution to shrinkage and the temperature-rise problem. Pulsing can be precisely controlled in nanoseconds. Interrupting the laser beam allows the target material to cool between laser pulses, thus preventing overheating. Few studies compared argon and pulsed laser, but, since the dye laser is a different instrument from the argon laser, it is difficult to conclude whether its results were due to pulsing of the laser bean or use of a different laser.[10,12]

Many light polymerized composites contain only CQ as photoinitiator for the generation of free radicals and free radical polymerization reaction.[5] Some composites contain CQ and other photoinitiators, known as coinitiators, which absorb light at shorter wavelengths (<410 nm). Some LED curing units have very narrow absorption spectra compared with halogen units (390-530 nm). The absorption of shorter wavelengths within the composite is greater than for longer wavelengths, which results in an altered light spectrum in depth of the composite.[20] The shorter wavelengths, necessary for excitement of the co-initiators, is strongly reduced at greater depths within the composite. Therefore, the co-initiator is probably not excited to a great extent at these deeper regions and does not contribute significantly to the polymerization reaction.[20]

The typical degree of conversion of Bis GMA-based dental resins exposed to a halogen or LED device ranges from 43% to 75%.[3,7,21-22] The newest generation of LED units has some broader spectrum (460-490 nm) than the first generation of LED units. However, the maximum irradiance for a blue diode laser is 474 nm. It is relevant to point out that the most efficient wavelength to excite CQ is around 470 nm and, therefore, the blue diode laser is shown to be more efficient, regardless of its reduced irradiance. The unwanted wavelengths do produce additional heat, affecting the kinetics of the reaction and may thereby influence the reaction.[3,22]

The range of the degree of conversion values obtained in this study varied from 57% to 69% for TC and 45% to 63% for TEC. From these results, it is obvious that, in the case of both materials, the results are almost identical when polymerized with Bluephase 16i light source regardless of the B16S or B16H polymerization mode used. This can be linked to the intensity of both modes: both have an intensity of 1600 mW/cm^2, but only the B16H mode has the stated intensity during all 10 seconds of polymerization, and the B16S mode only has this intensity during the last 10 seconds, while, for the first five seconds, it has a doubly lower intensity. In polymerization with the diode laser, the degree of conversion increases an average of 2% as time of illumination increases. However, for complete evaluation of efficiency of the diode laser as a light source for photopolymerization of composite materials and comparison with the widely used LED device, it would be necessary to examine temperature rise during polymerization and polymerization shrinkage as key parameters for evaluating polymerization quality.

When observing the tested composite materials, it is obvious that TC, as a fine particle hybrid, exhibits a greater degree of conversion than TEC, a nanohybrid composite material, regardless of the light source used. From Table 1, TC and TEC can be seen as differing in the amount of inorganic and organic filler and in the size of filler particles, which points to the fact that the degree of conversion greatly depends not only on the intensity of the light source but also on the composition of the composite material. According to the manufacturer, TC has CQ as a photoinitiator, while TEC has CQ and TPO, with an absorption spectra between 390 and 430 nm. Bluephase 16i, according to the manufacturer, has a spectrum between 430 and 490 nm, while the blue diode laser has a spectrum at 474 nm. This may explain the lower degree of conversion values in the case of polymerization of the TEC composite material with each tested light source.

A very high degree of conversion was achieved during sample polymerization using the diode laser for only 20 seconds of illumination. Development of technology in the area of light sources presupposes shortening curing time, which, as a consequence, has increased intensity of the LED device. Because of the higher intensity, it is necessary to install filters, which instantly points to the question of the temperature rise and diodes as a "cold light source." It is necessary to evaluate whether is it more essential to shorten polymerization time and increase intensity, which will cause greater temperature rise or if is it better to maintain the polymerization period with lower intensity and in a way that lowers the temperature rise and the negative consequences of quick polymerization of the composite materials, such as polymerization shrinkage and stress.

For future research, a big question remains to be answered: if LEDs with high intensity and very short curing time produce heat, can they still be regarded as a cold light source, and what are their advantages compared to halogen curing units?

CONCLUSIONS

Lasers have been promoted for resin curing, but their high costs and technique sensitivity have limited their use. The results of this study show that low powered blue diode laser devices satisfy the degree of conversion compared to the newer generation of high power LED curing units. However, because of their construction, low powered blue diode laser devices are still not available for clinical use. In the near future, rapid technology development will probably result in the use of diode blue lasers not only in experimental conditions but also in everyday clinical practice.

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