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Composite Depth of Cure Obtained with QTH and LED Units Assessed by Microhardness and Micro-Raman Spectroscopy

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Clinical Relevance

Lower depth of cure with the LED unit, compared to the QTH unit, is associated with different light scattering due to differences in spectral emission.

SUMMARY

This study analyzed the depth of cure of a composite assessed by microhardness and the degree of conversion as a function of the light cure unit (LCU) used. Two light cure units, one LED (Ultraled–Dabi Atlante) and one quartz-tungsten-halogen (QTH, Optilux 401–Demetron) unit were used to cure 4.0 x 4.0 mm and 5.0 mm deep composite specimens (Filtek Z250, 3M ESPE). After 24 hours storage at 37°C, Knoop microhardness and degree of conversion were measured on the irradiated surface and at each millimeter of the sample's depth. The degree of conversion was determined by using micro-Raman spectroscopy. The specimens cured with the QTH unit presented uniform decay in microhardness up to 4 mm in depth. Beyond 4 mm, the drop was abrupt. With LED photoactivation, uniform decay was observed only up to 2 mm. At higher depths, the decay in microhardness increased rapidly, especially beyond 3 mm. Depth of cure assessed by micro-Raman revealed that the degree of conversion behaved similarly to microhardness for both LCUs. A strong linear regression between microhardness and the degree of conversion, including both LCUs, was established with R^2=0.980.

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INTRODUCTION

Recently, a new technology based in blue light emitting diode (LED) was introduced to cure dental composites. LED technology differs from QTH by the spectral emission that favorably matches the absorption spectrum of camphoroquinone.[1]

The degree of conversion of resin composites is directly related to their mechanical properties. Among them, microhardness values have shown a strong correlation with the degree of conversion measurements obtained by vibrational methods, such as Fourrier-transformed infra-red spectroscopy (FTIR)[2] and FT-Raman spectroscopy (FTIR).[2-4] Micro-Raman spectroscopy has advantages, including allowing spectral analysis of very small areas of the sample (in a micrometric scale) without requiring any special sample preparation.[3,5-6] In unfilled resins, a previous study showed strong linear correlation between microhardness and degree of conversion. However, the authors noticed that a specific conversion value cannot be assigned to a hardness number, since the latter varies with filler content and matrix composition.[7] Notwithstanding, the association of microhardness and spectroscopy techniques may be advantageous, since a study found that Raman spectroscopy is more sensitive to changes in the first stages of curing reaction, while microhardness is more sensitive for detecting small changes after the network is crosslinked.[8]

This study accessed the depth of cure of a hybrid composite achieved with QTH and LED photo-activation units by means of Knoop microhardness and degree of conversion measurements using micro-Raman spectroscopy. The hypothesis tested was that Knoop microhardness is a valid test indicative of degree of conversion regardless of the LCU used.

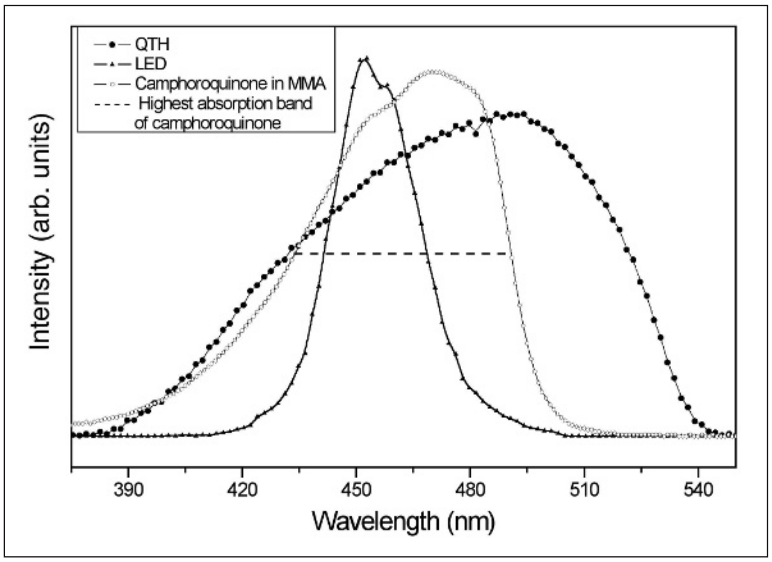

Figure 1. *Spectral distribution of the two different light curing units, plus the spectrum of the camphoroquinone in methylmetacrylate (MMA).*

METHODS AND MATERIALS

A shade A3 hybrid composite (Filtek Z250, 3M ESPE, St Paul, MN, USA) was used in this study. Two light curing units (LCU) were used: a quartz-tungsten-halogen (QTH) bulb unit (Optilux 401, Demetron, Danbury, CT, USA) with an output irradiance of 550 mW/cm^2 and a light-emitting diode (LED) unit (Ultraled, Dabi Atlante Ltda, Ribeirão Preto, SP, Brazil) with output irradiance of 360 mW/cm^2. The spectra of both LCUs is shown in Figure 1. Irradiances were measured using a hand-held radiometer (Model 100, Demetron).

Specimens (n=5) were obtained inserting the composite in a single increment into a stainless steel mold with a 4 x 4 mm cross-section and a depth of 5 mm. Photoactivation was performed by positioning the tip of the light guide onto the top surface of the composite and covering it with a mylar strip. Irradiation time was 40 seconds for both LCUs, resulting in radiant exposures of 22 J/cm^2 for the QTH unit and 14 J/cm^2 for the LED unit. After photoactivation, the specimens were removed from the mold and stored dry, in the dark, at 37°C for 24 hours.

Degree of Conversion Measurement

After the storage period, three of the five specimens were randomly selected for degree of conversion (DC) measurement. DC was determined at six different depths: top, 1, 2, 3, 4 and 5 mm. The measurements were performed at the lateral surface of the composite using a Micro-Raman spectrometer (model 2200, Renishaw, Gloucestershire, UK). Samples were excited at 633 nm using a He-Ne laser beam with a focal area of 1.0 µm diameter. Spectra were recorded at a 2.0 cm^{-1} resolution. The ratio of vibrational bands of the residual non-polymerized methacrylate C=C stretching mode at 1640 cm^{-1} to the aromatic C=C stretching mode 1610 cm^{-1} was calculated, together with the ratio of the uncured composite. The degree of conversion (DC) was calculated by the following equation:

$$DC(\%) = \left\{ 1 - \left[\frac{R_{\,polymerized}}{R_{\,unpolymerized}} \right] \right\} \times 100$$

where R is the ratio between the band height at 1640 cm^{-1} and the band height at 1610 cm-1. Figure 2 displays the two bands for two different degrees of conversion.

Knoop Hardness Measurement

The specimens were sanded parallel to their longitudinal axis with 600 and 1200 grit SiC paper to provide a smooth, flat surface. Knoop hardness (KHN) was measured in a microhardness tester (model HMV-2/2

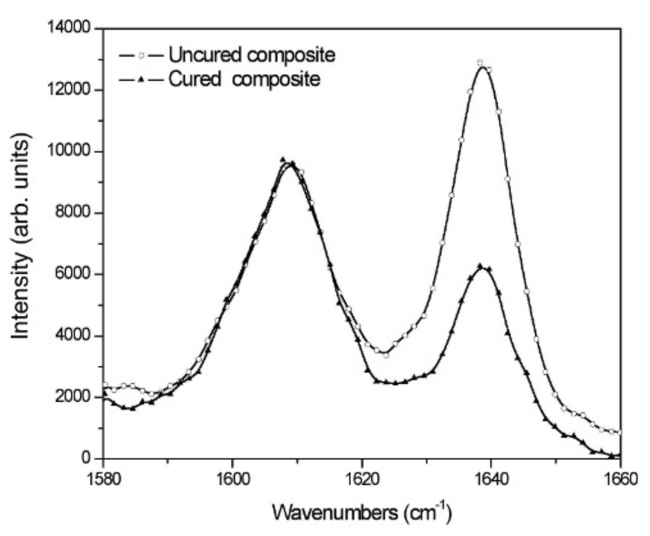

Figure 2. *Raman spectra of C=C aliphatic stretch band around 1610 cm-1 and residual aromatic C=C stretch band around 1640 cm-1.*

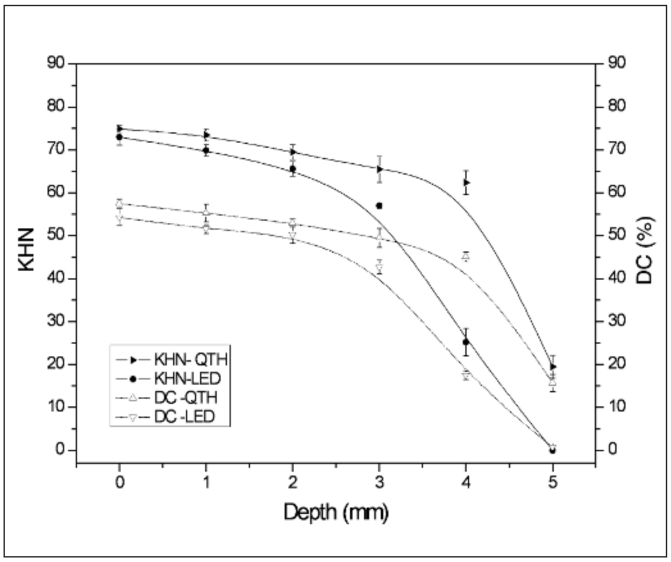

Figure 3. *Degree of conversion and microhardness means as function of specimen depth. Error bars represent standard deviation (SD) (KHN: Knoop hardness number; DC: degree of conversion; QTH: quartz-tungsten-halogen unit; LED: light-emitting diode unit).*

T, Shimadzu, Kyoto, Japan) using a 50 g load for 30 seconds. Three indentations were made at the same depths described for the micro-Raman test.

DC and KHN data were submitted to two-way ANOVA/Tukey's test with a global significance level of 5%. Also, linear regression analysis was conducted with both variables.

Resin Composite Transmittance Measurements

In order to analyze the composite transmittance spectrum, a sample was obtained in a stainless steel matrix 10 mm in diameter and 0.75 mm in height. The matrix was placed on a microscope glass slide that was slightly overfilled with composite and covered with another glass slide. The composite was cured with a conventional LCU (Optilux 401) for 40 seconds. Light transmission through the composite between a 400 and 800 nm wavelength was measured by the UV-Visible spectrophotometer, Cary 1E (Varian, Palo Alto, CA, USA).

RESULTS

Table 1 and Figure 3 show KHN and DC results as a function of specimen depth for both LCUs. It can be observed that, for the QTH and LED units, no significant difference in KHN was detected up to 1.0 mm. For the QTH unit, at higher depths up to 4 mm, hardness dropped slightly, decreasing abruptly between 4.0 and 5.0 mm. For the LED unit, KHN was significantly but slightly reduced as much as 2.0 mm, and a severe drop was observed in depths beyond 2.0 mm. At the 5.0 mm depth, KHN measurement was not possible due to insufficient curing. Composite behavior in terms of DC was very similar to that described for KHN. Slight gradual reductions in DC up to 4.0 mm for the QTH unit and up to 3.0 mm for the LED unit were recorded. Beyond those depths, DC dropped severely.

Figure 4 shows the results of the linear regression of KHN as a function of DC for each LCU. The regression for both LCUs was statistically parallel and coincident, allowing for a unique regression equation including both LCUs.

The transmittance spectrum of a flat layer of

Table 1: *KHN and DC Averages and Standard Deviations as a Function of Specimen Depth for Each Light Curing Unit**

Depth of Cure (mm)	KHN		DC (%)	
	QTH	LED	QTH	LED
0.0	74.9 (0.8)[a]	73.0 (1.9)[abc]	57.5 (1.0)[a]	54.3 (1.9)[abc]
1.0	73.5 (1.4)[ab]	69.9 (1.3)[bc]	55.3 (2.0)[ab]	51.6 (1.0)[bcd]
2.0	69.5 (1.7)[c]	65.6 (1.7)[d]	53.0 (0.9)[bcd]	50.2 (1.9)[cd]
3.0	65.5 (3.0)[d]	57.0 (0.6)[e]	49.5 (2.2)[d]	42.7 (1.6)[e]
4.0	62.4 (2.8)[d]	25.2 (3.2)[g]	45.1 (1.1)[e]	17.5 (1.0)[f]
5.0	19.5 (2.6)[g]	0.0 (0.0)[h]	15.7 (2.0)[g]	0.7 (0.6)[h]

**In each test, the averages followed by the same letters are not significantly different (p<0.05).*

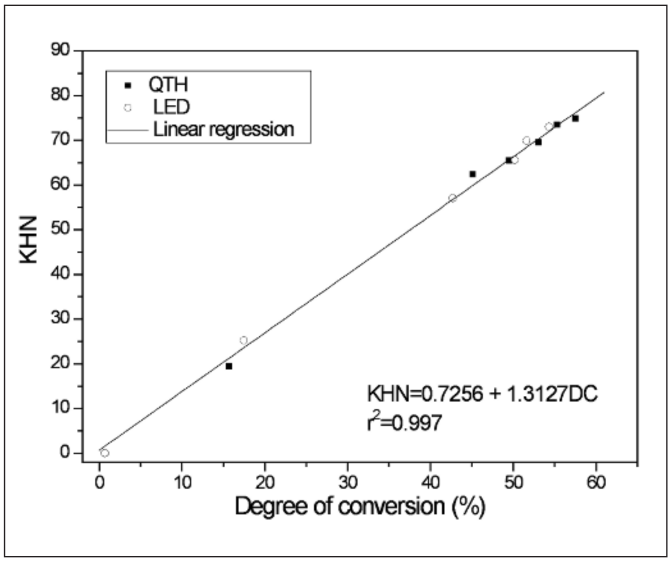

Figure 4. *Linear regression analysis of microhardness (KHN) as a function of the degree of conversion (%) measured between 0 (top) and 5 mm depths.*

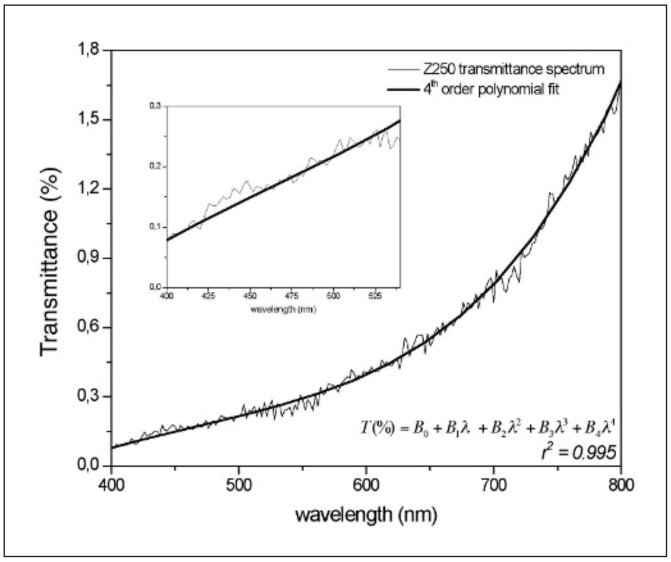

Figure 5. *Transmittance spectrum of a 0.75 mm thick layer of polymerized composite, corrected by blank and polynomial fit to a fourth order. Equation coefficients:* B_0=-0.9001, B_1=8.864x10^{-4}, B_2=1.503x10^{-5}, B_3=-4.0552x10^{-8}, B_4=3.1730x10^{-11}.

0.75 mm of polymerized composite shows a high dependence on the wavelength. This dependence fits extremely well into a fourth order polynomial, with R^2=0.995, as seen in Figure 5.

DISCUSSION

Several reports are found in the literature regarding the correlation between microhardness and degree of conversion.[5,7-8] Though hardness presents a good correlation with DC for a specific resin, hardness values cannot be used to predict DC when different resins are compared.[7] In this study, both KHN and DC values did not vary significantly up to a 1.0 mm depth regardless of the LCU considered. However, slightly lower values were obtained with the LED unit. Moreover, beyond 2.0 mm, KHN and DC values dropped faster for the LED unit than for the QTH unit. Up to 2.0 mm depth, the QTH unit presented a KHN reduction rate of approximately 2.7 units per mm, while for the LED unit, microhardness decreased approximately 3.7 units per mm.

These values are not in agreement with a previous study that found a reduction gradient of more than 10 KHN/mm up to a 2 mm depth, probably because of the dark composite used and the low power density of the light cure unit.[9] Other studies have demonstrated lower gradients of KHN, between 1.8 and 2.5 units per mm up to a depth of 2.0 mm, depending on the composite tested. Darker shades and more heavily filled composites presented a more severe gradient.[5,10] The lower reduction of KHN/mm reported in the recent literature is probably related to improvements in composites composition, spectral emission and irradiance of photoactivation units.[11]

Regardless of the method used for determining the depth of cure, it was observed that the results were significantly lower for the LED unit than for the QTH unit.[12] Two different reasons can possibly explain this feature. First, the fact that the radiant exposures were different (22 J/cm^2 for the QTH and 14.4 J/cm^2 for the LED unit). Nevertheless, it can be observed that, even considering that the radiant exposures differ by more than 1.5 times, neither DC nor KHN values differ significantly between LCUs up to a depth of 2.0 mm.

At higher depths, the difference between the LCUs could be explained by the fact that restorative resin composites are composed of an organic matrix that is transparent for visible light, and a filler fraction, which is a highly light-scattering material. The light-scattering phenomenon translates the relationship that exists between the wavelength of the light source and the dimensions of the scattering material according to the Rayleigh or Mie effects. While the former deals with particles of magnitude similar to or smaller than the light wavelength, the latter is related to particles larger than the light wavelength. The threshold between the Rayleigh and Mie effect domains are tenuous; however, considering the average wavelength emitted by dental LCUs and the average particle size of the composite tested (0.6 µm), the Rayleigh scattering equation could be applied.[13]

Light scattering is often measured by the scattering cross section (σ), defined as the area upon which enough energy falls from the plane wave to equal the scattered intensity. Considering the Rayleigh scattering, the cross section (σ) is proportional to the inverse of the fourth power of the wavelength (λ), as shown:

$$\sigma \propto \frac{1}{\lambda^4}$$

This means that, the smaller the wavelength, the higher the cross section and, consequently, the higher the scattering.[13] Even if the size of the filler in the composite, compared to the wavelengths of both LCUs, makes the Rayleigh scattering somewhat of an approximation, the transmittance spectrum determined on a 0.75 mm layer of polymerized composite shows a high dependence on the wavelength (Figure 5). This feature means that the transmitted light through the composite falls extremely fast for low wavelengths.

From Figure 1, it can be observed that the camphoroquinone absorption band has a broad spectrum going from 390 nm to 510 nm. Considering that the region of highest absorption is the spectral width at half of the absorption peak height, the authors observe an interval between 434 and 491 nm (Figure 1, dashed line). In this spectral range, the LED unit has the greatest part of the emitted spectrum centered on 453 nm, while for the QTH unit, it is around 491 nm.

The difference in wavelengths from 491 nm (QTH) to 453 nm (LED) represents an increase in light scattering of more than 38% obtained by the relation: % of scattering increase = $\lambda_{halogen}^4/\lambda_{LED}^4$. This means that, at deep portions of the composite specimen, due to the scattering promoted by the filling, LED irradiance drops more severely than irradiance of QTH.

CONCLUSIONS

The QTH unit presented a gradual reduction in KHN and DC up to a depth of 4.0 mm for the studied composite, while for the LED unit, a more severe drop in these variables was observed beyond a depth of 2.0 to 3.0 mm. A strong linear regression was observed between DC and KHN, regardless of the LCU. Finally, the high light scattering caused by the composite filler for low wavelengths may explain the higher DC and KHN in higher depths shown by the QTH unit compared to LED.

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