Energy dependent polymerization of resin-based composites

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Chapter 5

Polymerization efficiency of tungsten-halogen and LED lamps: A universal energy conversion relationship predictive of conversion of resin-based composite.

Introduction

Studies exploring the photopolymerization of resin-based composite (RBC) have shown that conversion and depth of cure is dependent upon the energy of exposure (Cook, 1980; Nomoto, Uchida, & Hirasawa, 1994; Halvorson, Erickson & Davidson, 2002). In recent work, an energy-conversion relationship (ECR) was defined for RBC using Fourier Transform Infrared Spectroscopic (FTIR) analysis of photopolymerized RBC and the light transmitting properties of the RBC (Halvorson, Erickson & Davidson, 2003). This ECR described the energy associated with a specific conversion at any depth within a cylinder of the photopolymerized RBC. Further, it was shown that there was reciprocity between time and incident power density so that the ECR uniquely defined the conversion with depth for any incident exposure energy. Coupled with the transmission properties of various shades of the RBC, the ECR could also be used to reliably predict conversion as a function of depth (conversion profile) for any shade with this RBC family of materials. Depth of cure, as defined by the scrape-back method (International Organization for Standardization, 2000) has also been investigated (Halvorson & others, 2002) and an energy associated with the scrap-back length of a photopolymerized RBC was determined and defined as the critical scrape-back energy ($E_c$). This $E_c$ was used to successfully predict the scrape-back length of cylinders of RBC for various incident energies and shades of RBC. While the ECR, as described, has been shown to have predictive capability that makes it useful, it has the limitation that it is valid only for the light source used to generate it. It would be beneficial to have an ECR that can be used with any light source to describe the conversion characteristics of RBC.

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During photopolymerization, the spectral dependence of the energy absorbed by the RBC photosensitizer is a function of the product of the spectral absorbance of the photosensitizer and the spectral irradiance of the light source. This relationship will be different for each light source and could be used to define the relative energy efficiencies of different light sources. A universal ECR might then be defined that could be used to describe RBC conversion characteristics for any light source by using the light source efficiency as an energy conversion factor. Similarly, conversion characteristics obtained with one light source could be used to predict the characteristics for another light source by an energy conversion using the ratio of light source efficiencies.

The light source/photosensitizer combination most typically used to photopolymerize RBC is the tungsten-halogen incandescent lamp and camphorquinone (CPQ). The emission of tungsten-halogen lamps designed for dental use is filtered to pass radiation of wavelengths between 400 and 500nm, corresponding to the carbonyl absorbance of CPQ. There is, however, a significant variation in the spectral distribution of such lamps (Cook, 1982), presumably due to filter composition. Recently, lamps based on light emitting diodes (LED) have become available for dental use. This technology eliminates the need for filtration since the emission is electronically and not thermally generated. The resulting spectral bandwidth of LED lamps is relatively narrow with a peak intensity typically occurring near the maximum absorbance of CPQ at 470nm (Mills, Jandt & Ashworth, 1999; Kurachi & others, 2001).

The objectives of the present investigation were to derive a universal energy-conversion relationship (ECR_u) predictive of RBC conversion characteristics and suitable for use with any light source by means of an efficiency factor for the light source; to use this universal energy scale to predict scrape-back lengths for RBC polymerized with both a tungsten-halogen and light-emitting diode (LED) light source and to experimentally verify those predictions; and to predict and experimentally verify a conversion profile for RBC polymerized with the LED light source.
Materials and Methods

Energy conversion relationship for photopolymerization with a tungsten-halogen lamp

Construction of the ECR for a tungsten-halogen lamp was described previously (Halvorson & others, 2002) and will be summarized below. A small particle hybrid resin-based composite (RBC) (3M™ESPE™Z100 Restorative, shade A3.5, 3M ESPE, St. Paul, MN, USA) was used throughout this study. The RBC was packed into a split stainless-steel mold producing a cylindrically shaped sample approximately 6mm in diameter by 16mm in length. Two stainless steel wedges positioned on opposite sides and along the full length of the mold permitted splitting of the cured sample down its length. Transparent polyester film was placed over the openings of the mold and a light guide from a tungsten-halogen lamp (3M™ESPE™XL 3000 Curing Lamp, 3M ESPE, St. Paul, MN, USA) was placed over one of the ends. The sample was exposed for sixty seconds with the lamp adjusted, using a variable transformer, to match the nominal power density of 250 mWcm\(^2\) (13,300mJcm\(^{-2}\) actual energy density) for the LED lamp (3M™ ESPE™ Elipar™ FreeLight, 3M ESPE, St.Paul, MN, USA). The radiation energy density of the curing lamp was determined using a power meter (Power Max 500D Laser Power Meter, Molelectron Detector Inc., Portland, OR, USA) integrating the radiant power density over the exposure time. Power density was determined by dividing the measured power by the cross sectional area of the light guide. After storing at room temperature for 24 hours, the sample was split and specimens dissected along its length for analysis using transmission FTIR microspectroscopy. Specimens were placed on a KBr disc and measured in transmission with a Nic-Plan™ Microscope combined with a Magna-IR® 750 spectrometer (Nicolet, Madison, WI, USA) coadding 90 scans at a resolution of 4cm\(^{-1}\). Three cylinders were prepared and analyzed for each group with three to five specimens measured at each depth. Conversion was determined by measuring the decreasing absorbance of the methacrylate carbon double-bond vibration at 1638cm\(^{-1}\) using as an internal reference the aromatic skeletal absorbance from Bis-GMA at 1582cm\(^{-1}\). Integrated areas of both peaks were determined using a standard baseline technique.

The transmittance \((T=P/P_0)\) was determined by polymerizing the RBC in 6mm diameter stainless steel molds of various lengths. The polymerized
sample together with its mold was placed on the detector of a power meter
(351 Power Meter, UDT Instruments, Baltimore, MD, USA) centering the
light guide of the curing lamp over the mold and in contact with the
sample. The power measured in this fashion \( (P) \) was divided by the
unattenuated power \( (P_0) \) obtained by placing the light guide in direct
contact with the detector head. A minimum of three replications was done
for each condition and a mean value was determined. Transmission as a
function of thickness was determined by regression analysis of the data.

The energy exposure at depths \( (E_d) \) where FTIR specimens were dissected
was determined from the incident energy \( (E_i) \) and the transmittance \( (E_d =
%T_d \times E_i) \). This permitted conversion to be related to energy and thereby
define an ECR for the test material.

\textit{Lamp efficiency}

The relative efficiencies of the tungsten-halogen lamp and LED lamp
were expressed relative to a hypothetical standard light source having
uniform spectral output of unity over the range of CPQ absorbance. The
output of this light source was multiplied by the CPQ spectral absorbance
normalized to unity at its peak absorption. The area of this process
defined a standard relative energy absorption and the standard light
source, by definition, would have an efficiency of 1.0. The spectral
emission curves of the tungsten-halogen and LED lamps were also
obtained and normalized to unity. These curves were similarly multiplied
by the normalized CPQ curve yielding areas that, when divided by the
standard area, gave the relative lamp efficiencies. The spectral emission
curves of the tungsten-halogen and LED lamps were determined using a
spectral radiometer (Model S2000, Ocean Optics, Dunedin, FL). The
spectral absorbance of CPQ was determined in ethanol using a UV-VIS
spectrometer (Model 8452A, Hewlett Packard, Palo Alto, CA).

\textit{Universal ECR}

A universal ECR \( (ECR_u) \) was constructed by defining a new energy scale
for the ECR previously described for the tungsten-halogen lamp. The new
energy scale was obtained by multiplying the previous scale by the
efficiency factor of the tungsten-halogen lamp. This universal ECR
represents the energy-conversion relationship for the hypothetical standard
lamp described earlier.
Conversion throughout the length of a cylinder of RBC polymerized with the LED lamp was predicted from the relative efficiency factor for the LED lamp and the universal ECR. First, the localized energy density through the length of RBC was determined using the transmission properties of the RBC (as described above) and the LED incident energy density. The product of the local energy density and the relative efficiency factor for the LED, scaled the energy density to the universal ECR where the conversion value was determined. The prediction was experimentally verified using the FTIR microspectroscopic method described above. An incident exposure of 13,300 mJcm$^2$ was used (60 second exposure with the LED lamp), as measured with the power meter as described above.

Scrape-back length: prediction and measurement

From previous measurements, a value of 32mJcm$^2$ was found for the critical scrape-back energy for the test material when exposed using the tungsten-halogen lamp described above (Halvorson & others, 2002). This value was obtained by determining the local energy density at the scrape back length from the incident exposure and transmission data. Using the relative efficiency factors and the critical scrape-back energy for the tungsten-halogen lamp, the critical scrape-back energy related to the LED lamp was predicted. This value was then used to predict scrape-back lengths for LED polymerized RBC at various energy densities. To experimentally verify the predicted scrape-back lengths, specimens were made by packing RBC into the cylindrical molds described above for FTIR sampling (without wedges). The RBC was exposed with the LED lamp at various energy densities achieved by using neutral density filters and modifying the exposure time. After 24 hours at room temperature, the molds were disassembled and the poorly polymerized material gently scraped off with a rigid plastic spatula and the resulting cylinder length measured. Three replicates were prepared and measured to the nearest 0.01mm. Scrape-back lengths were also predicted and experimentally measured for RBC polymerized with the tungsten-halogen lamp and compared to the values obtained with the LED lamp.
Results

Figure 1 shows the spectral distribution of the tungsten-halogen and LED lamps together with the spectral absorbance of CPQ, all on a normalized basis. The standard light source with an output of unity is also shown. Multiplying each light source by the CPQ absorbance yields the curves shown in Figure 2, which describes the spectral distribution of the relative energy absorbed by CPQ for each light source. The area corresponding to the standard light source gives the standard relative energy absorbed and defines an efficiency of unity. As expected, the areas for the LED and tungsten-halogen light sources are less than that for the hypothetical source and division by the area of the standard source provides efficiency factors of 0.50 and 0.39 respectively.

Figure 1. Normalized spectral emission of the tungsten-halogen and LED lamps together with the normalized spectral absorbance of CPQ. The standard light source with an output of unity is also shown.

Figure 2. Spectral distribution of the relative energy absorbed by CPQ for each light source.
Figure 3 shows the conversion profile of the RBC polymerized using the tungsten-halogen lamp with an incident energy density of 13,300 mJcm\(^2\). Transmission data was used to determine the energy density for each depth allowing the ECR associated with the tungsten-halogen lamp to be generated as shown in Figure 4. Multiplying this ECR by the relative efficiency factor for the tungsten-halogen lamp (0.39) yields the universal ECR also shown in Figure 4. The predicted conversion profile of RBC polymerized using the LED lamp, and the experimental values obtained with the same lamp are shown in Figure 5. The conversion profile for tungsten-halogen polymerized RBC (Fig. 3) is shown for comparison. The relative difference in lamp efficiency predicts the observed shift along the abscissa with equivalent energy exposures.

![Figure 3](image-url)  
*Figure 3.* Conversion profile of the RBC polymerized using the tungsten-halogen lamp. Incident energy density was 13,300 mJcm\(^2\).

![Figure 4](image-url)  
*Figure 4.* Energy conversion relationship (ECR) associated with the tungsten-halogen lamp (open circles). Multiplying this ECR by the relative efficiency factor for the tungsten-halogen lamp (0.39) yields the universal ECR for the standard lamp (solid line).

The relative difference in lamp efficiency also predicts a critical scrape-back energy of 24.4 mJcm\(^2\) for the LED lamp. Using this value, the predicted scrape-back curve for the LED lamp is shown in Figure 6a together with the predicted curve for the tungsten-halogen lamp and experimentally measured scrape-back lengths for four different exposure
energies. In Figure 6b, the scrape-back values are represented on the universal energy scale. The critical scrape-back energy for the universal energy scale corresponding to this curve is 16.3mJcm⁻².

**Figure 5.** Predicted conversion profile of RBC polymerized using the LED lamp, and the experimental values obtained with the same lamp. The conversion profile for tungsten-halogen (TH) polymerized RBC (Fig. 3) is shown for comparison.

**Figure 6a.** Predicted scrape-back lengths for the tungsten-halogen (TH) and LED lamps together with experimentally derived values.

**Figure 6b.** Scrape-back lengths measured for tungsten-halogen (TH) and LED lamps plotted after converting the incident energies of the lamps to that of the standard lamp.
Discussion

The results of this investigation have shown that a universal energy-conversion relationship (ECR_u) can be defined for a light-cured RBC that is predictive of conversion for any lamp, by characterizing the spectral efficiencies of the curing lamps relative to a standard light source. The choice of the standard light source is somewhat arbitrary but the one chosen allows for light sources that could possibly approach an efficiency of 1.0 but cannot exceed that value. The area for the standard light source is, by definition, simply the area under the normalized CPQ absorbance curve. It is implicit under this process that the quantum yield for free radical generation is wavelength independent. Therefore, at low conversions, conversion versus wavelength should mimic the CPQ spectral absorbance curve when equal quanta per wavelength are incident on a sample. This has generally been observed for RBC under exposure conditions yielding sub-maximal conversion (Nomoto, 1997).

The ECR produced in the present experiment using the tungsten-halogen lamp (Figure 4) was in very close agreement to the ECR described previously with the same lamp (Halvorson & others, 2003). While this ECR is sufficient to predict conversions for the LED lamp by comparing the LED lamp efficiency relative to the halogen lamp, it is more useful to express the ECR with respect to the standard lamp described. The reason being that others do not have access to this specific tungsten-halogen lamp, whereas, the standard light source proposed and the ECR_u for this specific RBC family can be used by anyone. It is only necessary to determine the relative efficiency of any light source being used and prediction of curing characteristics can be calculated. From the relative efficiencies of the lamps, it is predicted that, with an equivalent exposure, the LED lamp will cure RBC to greater depths than the tungsten-halogen lamp (Figure 5). The experimental results verify this prediction. Due to the exponential decay of light through RBC, the 31 percent greater measured efficiency for the LED lamp does not result in a proportional increase in cure depths. This is observed from inspection of the conversion profiles in Figure 5 as well as the comparison of scrape-back depths in Figure 6a, the latter showing only around six percent greater scrape-back length for the LED lamp. Similar differences in cure depths have been reported for RBC polymerized with approximately equivalent doses from an LED and tungsten-halogen lamp (Mills & others, 1999).
Although the efficiency of the LED lamp is greater than the tungsten-halogen lamp, a benefit in cure depth is only realized when the tungsten-halogen lamp is operated at reduced power levels. Since the tungsten-halogen lamp was operated at roughly fifty percent of its maximum output, its cure times could be reduced by approximately half when operated at full output and achieve the corresponding cure depths reported here, consistent with the reciprocity previously determined (Halvorson & others, 2002). Therefore, lamp efficiency, as defined here, together with maximum irradiance must be considered when evaluating the ultimate curing potential of different lamps. A measure of the photocuring efficiency inclusive of lamp irradiance has been derived from a kinetic expression for depth of cure (Cook, 1986).

The prediction of scrape-back lengths found in this experiment for RBC polymerized with the tungsten-halogen lamp verifies previous results where a critical scrape-back energy of 32mJcm$^2$ was used (Halvorson & others, 2003). From relative lamp efficiencies, a critical scrape-back energy of 24.4mJcm$^2$ for the LED predicts slightly greater scrape-back lengths for an equivalent exposure as shown in Fig 6a. For both lamps, the scrape-back length corresponds to approximately 20 percent conversion as observed from Figure 4, and is consistent with previous results (Halvorson & others, 2003). Scaling the exposure energy with respect to the hypothetical lamp places the scrape-back values for both lamps on the universal energy scale and the scrape-back lengths for both lamps converge on a single curve (Figure 6b). This curve represents a critical scrape-back value of 16.3mJcm$^2$. Using this value, together with relative lamp efficiencies provides a means for obtaining the critical scrape-back value for other lamps and consequently predicting associated scrape-back lengths.

Predicting conversion and depth of cure from the ECR’s and critical scrape-back lengths presented here are expected to be subject to similar restrictions described previously (Halvorson & others, 2003). These restrictions involve, primarily, the effect of different mold geometries and mold composition on depth of cure (Fan & others, 1984) and differences due to polymerizing at other temperatures (Maffezzoli & others, 1994).

**Conclusion**

A universal energy-conversion relationship has been described that is
predictive of conversion of a resin-bonded composite (RBC) polymerized with any light source. The universal energy scale has also been described as predictive of scrape-back lengths for this RBC family when polymerized with any light source. Both predictions rely on characterization of lamp efficiencies in comparison to the described hypothetical light source.
References


