

# Describing Adequacy of Cure with Maximum Hardness Ratios and Non-linear Regression

M Bouschlicher • K Berning • F Qian

## Clinical Relevance

Redefined hardness ratios, based on extended cure intervals and maximum hardness when used in conjunction with non-linear regression, provide a readily available and accurate characterization of the curing performance of LCU-composite combinations, which is superior to the use of traditional per-specimen hardness ratios. It is recommended that the light curing guidelines provided to clinicians should be based on this more accurate description of curing behavior.

## SUMMARY

**Knoop Hardness (KH) ratios (HR)  $\geq 80\%$  are commonly used as criteria for the adequate cure of a composite. These per-specimen HRs can be misleading, as both numerator and denominator may increase concurrently, prior to reaching an asymptotic, top-surface maximum hardness value ( $H_{MAX}$ ). Extended cure times were used to establish  $H_{MAX}$  and descriptive statistics, and non-linear regression analysis were used to describe the rela-**

**tionship between exposure duration and HR and predict the time required for  $HR-H_{MAX} = 80\%$ . Composite samples 2.00 x 5.00 mm diameter ( $n=5/grp$ ) were cured for 10 seconds, 20 seconds, 40 seconds, 60 seconds, 90 seconds, 120 seconds, 180 seconds and 240 seconds in a 2-composite x 2-light curing unit design. A microhybrid (Point 4, P4) or microfill resin (Heliomolar, HM) composite was cured with a QTH or LED light curing unit and then stored in the dark for 24 hours prior to KH testing. Non-linear regression was calculated with:  $H=(H_{MAX}-c)(1-e^{-kt})+c$ ,  $H_{MAX}$  = maximum hardness (a theoretical asymptotic value),  $c$ =constant ( $t=0$ ),  $k$ =rate constant and  $t$ =exposure duration describes the relationship between radiant exposure (irradiance x time) and HRs. Exposure durations for  $HR-H_{MAX}=80\%$  were calculated. Two-sample  $t$ -tests for pairwise comparisons evaluated relative performance of the light curing units for similar surface x composite x exposure (10-90s). A good measure of goodness-of-fit of the non-linear regression,  $r^2$ , ranged from 0.68-0.95. (mean = 0.82).**

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**Microhybrid (P4) exposure to achieve  $HR-H_{MAX} = 80\%$  was 21 seconds for QTH and 34 seconds for the LED light curing unit. Corresponding values for microfill (HM) were 71 and 74 seconds, respectively. P4  $HR-H_{MAX}$  of LED vs QTH was statistically similar for 10 to 40 seconds, while HM  $HR-H_{MAX}$  of LED was significantly lower than QTH for 10 to 40 seconds. It was concluded that redefined hardness ratios based on maximum hardness used in conjunction with non-linear regression provides an improved method of evaluating curing performance relative to traditional per-specimen hardness ratios.**

## INTRODUCTION

Manufacturers of both light curing units and resin composites typically recommend exposure times that presumably result in the adequate cure of a 2 mm increment of composite. Curing light marketing claims often stress very short cure intervals, which are presumably possible with higher irradiance ( $mW/cm^2$ ), while recommended curing times for composites are typically longer and presumably result in optimum polymerization of a specific product. Verifying marketing claims that curing lights with higher irradiance adequately cure resin composites with much shorter cure intervals has become a greater challenge with the plethora of new curing lights being introduced. As the inadequate polymerization of resin composites leads to decreased physical properties, increased wear, increased solubility with leaching of unreacted monomer and increased toxicity, it is of paramount importance that the practitioner use exposure times that ensure optimum polymerization.<sup>1-7</sup> Direct assessment of the degree of conversion (DC) includes infrared spectroscopy,<sup>8</sup> Raman spectroscopy<sup>9</sup> and micro-Raman spectroscopy,<sup>10</sup> but these methods require expensive equipment and expertise that is not always readily available. The degree of conversion (DC) of resin composite can be indirectly assessed by depth of cure measurements, such as microhardness profiles, scrape-back and visual tests, although the latter two tests overestimate depth of cure when compared with acceptable hardness and degree of conversion values.<sup>11</sup> Hardness is highly correlated with degree of conversion<sup>8</sup> and is more sensitive than FTIR at high levels of conversion, where it is sensitive to small changes in polymer cross linkages.<sup>3</sup> The bottom:top-surface hardness ratio of 2 mm thick resin composite samples  $\geq 0.80$  has commonly been used to operationally define adequacy or sufficiency of cure.<sup>12-13</sup> It has been shown that hardness ratios correlate well with the bottom-to-top degree of conversion ratios as measured with Fourier Transform Infrared Spectroscopy (FTIR).<sup>5</sup> However, hardness ratios may be a misleading indicator of adequacy of cure when cal-

culated from a range of exposures where the top surface is not fully polymerized. Early in the exposure, both the numerator and denominator of the hardness ratio may be increasing concurrently, and the ratio may remain relatively constant over an extended range of exposure times.<sup>14</sup>

Since the top surface of the composite is the most highly irradiated, insufficient conversion of this surface has generally not been a concern. Near maximum conversion values have been obtained with low irradiance and short exposure times.<sup>15</sup> It is generally assumed that the top surface of a resin composite reaches maximum hardness early during the radiant exposure and, once cured, it does not get much harder. A reciprocal relationship exists between irradiance ( $mW/cm^2$ ) and exposure time, and the extent of polymerization is related to the product of these numbers, radiant exposure ( $mJ/cm^2$ ). Since the irradiance of most curing lights is fixed (assuming a fixed distance between the light guide and the composite), exposure time is the variable that controls the radiant exposure and, hence, the extent of polymerization. Extended exposure times and higher radiant exposures result in improved Knoop hardness, especially for surfaces with increased depth, but both top and bottom surface hardness increases with prolonged irradiation times.<sup>16</sup>

Murray and others<sup>14</sup> compared the curing effectiveness of five high-intensity LED curing lights to a QTH control using four contemporary resin composites cured with an extended range of exposure times (10-180 seconds). Sufficiency of cure was defined as a hardness ratio  $\geq 0.80$ . There was little difference in the hardness ratios achieved among the various curing lights, as both top-surface KHN and bottom-surface KHN increased concurrently through a broad range of exposure durations (10 seconds to 180 seconds). However, there were significant differences and ordinal ranking trends among the various curing lights when absolute top and absolute bottom KHN values were compared.<sup>14</sup> These findings suggest that per-specimen hardness ratios may be a relatively insensitive measure for comparison testing of curing lights or the curing characteristics of specific composites. Absolute KHN values in the context of maximal top or bottom surface KH numbers also need to be considered when assessing adequacy or sufficiency of cure.

A study by Leonard and others<sup>17</sup> examined the polymerization efficiency of three first generation LEDs compared to a conventional QTH by means of Knoop hardness testing. A linear regression of hardness ratios versus curing time was performed, and the regression equation was used to predict the light exposure necessary to result in a hardness ratio  $\geq 0.80$ . There was a significant correlation between exposure duration and hardness ratios ( $r^2$  range of 0.76-0.91,

mean 0.85). Upon examination of the correlation and linear regression analyses, it appeared that the hardness ratios remained relatively constant over a wide range of cure times; therefore, the minimal exposure time required to achieve a hardness ratio of 0.80 does not correspond with optimal DC.<sup>17</sup> It was also observed that linear regression was not the best description of the relationship between radiant exposure (irradiance x exposure duration) and hardness ratios. A 2004 study by the same authors proposed an alternative statistical description of the relationship between resin polymerization sufficiency and exposure duration.<sup>18</sup> Referring to their 2002 study, it was observed that the curvature in the early and late cure intervals data obtained for hardness ratios tended to be below the linear regression line. A non-linear regression model provided a better estimate of the exposure duration required to achieve adequate resin composite polymerization. A non-linear regression analysis, where top surface  $KHN_{MAX}$  is an asymptotic value and k is a rate parameter indexing how quickly that asymptote is approached, yielded a better statistical fit with higher  $r^2$  values ( $r^2$  averaged 0.94). They recommended that the use of hardness ratios for analysis of polymerization sufficiency on a per-condition or per-specimen basis should be abandoned and that bottom surface data should only be interpreted with respect to an asymptotic value of top-surface hardness.



The current study utilized a non-linear regression equation of B/T KH ratios generated from an extended range of exposure durations (10 to 240 seconds) to evaluate the composite cure characteristics of two composites and relative performance of an LED and QTH light-curing unit (LCU). Hardness ratios based on maximal top surface KHN values and bottom surface KH numbers were used to assess adequacy or sufficiency of cure, while demonstrating the utility of the method.

METHODS AND MATERIALS

Cylindrical molds, 2.00 mm height x 5.0 mm diameter, were slightly overfilled with uncured composite, covered by a Mylar strip and compressed with a glass microscope slide. The slide was removed and the distal end of the light guide was placed in contact with the Mylar strip.

Shade A2 resin composite specimens (Table 1) of Heliomolar (HM, Ivoclar Vivadent, Amherst, NY, USA) or Point 4 (P4, SDS/Kerr, Orange, CA, USA), were cured for 10 seconds, 20 seconds, 40 seconds, 60 seconds, 90 seconds, 120 seconds, 180 seconds or 240 seconds with each LCU (n=5/group). Exposure durations six times the manufacturer’s recommended cure time of 40 seconds were used to generate data points with radiant exposure values high enough that further increases in exposure time did not result in increased hardness numbers.<sup>14</sup> The high intensity LED and QTH light curing units (LCUs) evaluated (Table 1) were: Bluephase in High Power mode (BLU, Ivoclar Vivadent) and Demetron Optilux 501 with 8 mm Turbo Tip (DEM, SDS/Kerr, Danbury, CT, USA). The irradiance and absolute irradiance of each LCU (Figure 1) was measured with a USB 2000 spectrometer and FOIS-1 integrating sphere (Ocean Optics, Dunedin, FL, USA). Power and radiant exposure for the range of exposure durations were calculated and verified experimentally using the Ophir NOVA Laser Power/Energy monitor and StarCom Software (Ophir Optronics, Peabody, MA, USA). The integrated area under the curve was calculated to determine that power output was constant throughout the various exposure durations. Irradiance was monitored periodically throughout sample fabrication.

Following light curing, the samples were stored in the dark at 37°C with 100% humidity for 24 hours before KHN testing with a Micromet II Microhardness Tester

Table 1: Light Curing Units and Resin Composites Evaluated						
Light Curing Unit (LCU)	Manufacturer	Light Curing Unit (LCU)	Tip Diameter (mm)	Area (cm²)	Power (mW)	Irradiance (mW/cm²)
	Ivoclar Vivadent Amherst, NY, USA	Bluephase (BLU) high power mode	6.40	0.43	506	1,177
	SDS Kerr Danbury, CT, USA	Demetron Optilux 501 (DEM) 8 mm turbotip	7.64	0.46	633	1,379
Resin Composite	Manufacturer	Lot #	Shade	Particle Classification	Recommended Cure Time	Resin Composite
Heliomolar (HM)	Ivoclar Vivadent Amherst, NY, USA	541502AN	A2	Microfill	40 seconds	Heliomolar (HM)
Point 4 (P4)	Kerr Corporation Orange, CA, USA	29899	A2	Microhybrid	40 seconds	Point 4 (P4)

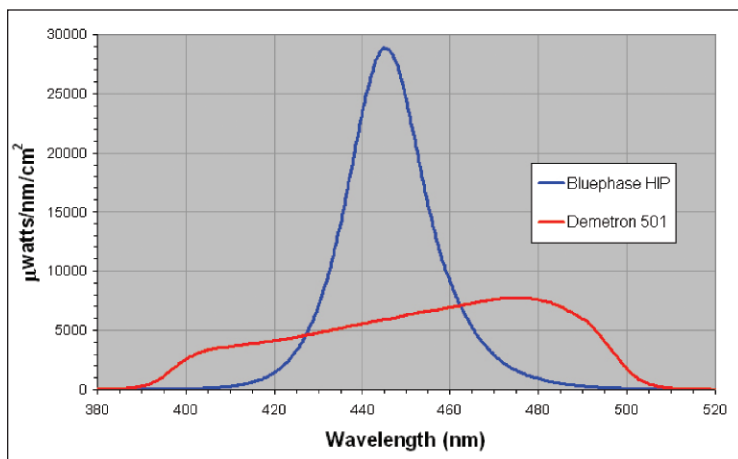


Figure 1. Absolute Irradiance of DEM & BLP HIP measured with Ocean Optics USB-2000 spectrometer with FOIS-1 Integrating Sphere.

(Buehler, Lake Bluff, IL, USA) using a 25g load applied for 12 seconds. Mean top and bottom surface microhardness values ( $n=3$ ) were calculated using the formula:  $KHN = L/(12 * Cp)$ , where  $L$  is the test load in grams,  $l$  is the dimension of the long axis of indentation chevron in micrometers and  $Cp$  is a constant relating  $l$  to the projected area of the indentation.<sup>19</sup>

Hardness ratios based on maximal top surface hardness ( $HR-Y_{MAX}$ ) were calculated from bottom hardness numbers and the corresponding maximal top-surface hardness value ( $Y_{MAX}$ ) for each respective composite/LCU combination. Descriptive statistics and non-linear regression of B/T hardness ratios versus exposure duration were performed to describe the relationship between  $HR-Y_{MAX}$  and radiant exposure. This, in turn, was used to predict the exposure duration required to produce an  $HR-Y_{MAX}$  of 80% for the test conditions.  $Y = (Y_{MAX} - c) (1 - e^{-kt}) + c$  is non-linear regression, where  $Y_{MAX}$  is the maximum hardness (an asymp-

totic value),  $c$  is a constant,  $k$  is a rate parameter describing how quickly the asymptote  $Y_{MAX}$  is approached and  $t$  is exposure duration. Maximum hardness ( $Y_{MAX}$ ) and the rate parameter ( $k$ , describing how quickly  $Y_{MAX}$  is approached) were estimated using the non-linear prediction equation with  $r^2$  indicating the proportion of the (corrected) total variation to be attributed to the fit. For top surfaces, both  $Y_{MAX}$  and  $k$  were estimated. For bottom surfaces,  $Y_{MAX}$  was fixed as the top-surface value and  $k$  was estimated under this constraint. Confidence Intervals (CI) of 95% were also determined for top  $Y_{MAX}$ , bottom  $Y_{MAX}$  and  $k$ . A two-sample  $t$ -test was performed to compare the relative performance of the two LCUs for similar surface x composite x exposure.

## RESULTS

Maximum hardness ( $H_{MAX}$ ) and rate parameter ( $k$ ), describing how quickly  $H_{MAX}$  is approached, are listed in Table 2, along with their corresponding 95% confidence intervals. The  $r^2$  values, indicating the proportion of the (corrected) total variation attributed to the fit, are also listed in Table 2.

Non-linear regression model fit  $r^2$  ranged from 0.68-0.95 (mean  $r^2 = 0.82$ ). For both the hybrid (P4) and microfill resin composite (HM), non-linear regression predicted that the LED light (BLU) would result in higher maximum top and bottom KH than use of the QTH light (DEM). When HM was cured with BLU, the estimated  $Y_{MAX}$  was 49.56 ( $r^2=0.68$ ) versus 46.7 ( $r^2=0.82$ ) with DEM, and the estimated maximum bottom hardness was 46.1 ( $r^2=0.95$ ) versus 42.0 ( $r^2=0.88$ ), respectively. P4, when cured with BLU, had an estimated  $Y_{MAX}$  of 70.1 ( $r^2=0.88$ ) versus 67.1 ( $r^2=0.74$ ) with DEM and an estimated maximum bottom KH of 68.8 ( $r^2=0.92$ ) versus 63.5 ( $r^2=0.79$ ), respectively (Table 2).

Table 2: Estimation of  $H_{MAX}$  and  $k$  in the Non-linear Prediction Equation:  $H = (H_{MAX} - c) (1 - e^{-kt}) + c$ , with  $r^2$  for Goodness of Fit

Composite	LCU	Surface	$H_{MAX}^*$	95% CI ( $H_{MAX}$ )		$k^{**}$	95% CI ( $k$ )		Model $r^2$
				Lower	Upper		Lower	Upper	
HM	BLU	T	49.56	46.64	52.49	0.0135	0.0038	0.0231	0.68
HM	DEM	T	46.70	44.97	48.43	0.0198	0.0105	0.0290	0.82
HM	BLU	B	46.14	44.64	47.64	0.0233	0.0181	0.0285	0.95
HM	DEM	B	42.03	40.30	43.75	0.0328	0.0191	0.0465	0.88
P4	BLU	T	70.12	68.66	71.57	0.0258	0.0175	0.0340	0.88
P4	DEM	T	67.11	65.76	68.46	0.0459	0.0211	0.0707	0.74
P4	BLU	B	68.77	67.19	70.34	0.0201	0.0146	0.0256	0.92
P4	DEM	B	63.52	62.11	64.93	0.0498	0.0214	0.0782	0.79

\* $H_{MAX}$  is maximum hardness.

\*\* $k$  is a rate parameter describing how quickly that asymptote is approached.



Table 3: Exposure Duration Needed to Achieve a Bottom-surface Hardness That is 80% That of Top-surface $H_{MAX}$ , Based on Inverse Regression			
Composite	LCU	Exposure Duration	Percentage*
HM	BLU	74.5	85.9
HM	DEM	71.2	88.9
P4	BLU	33.8	81.6
P4	DEM	21.0	84.5

\*Percentage of bottom-surface  $H_{MAX}$  that corresponds to 80% of top-surface  $H_{MAX}$ .

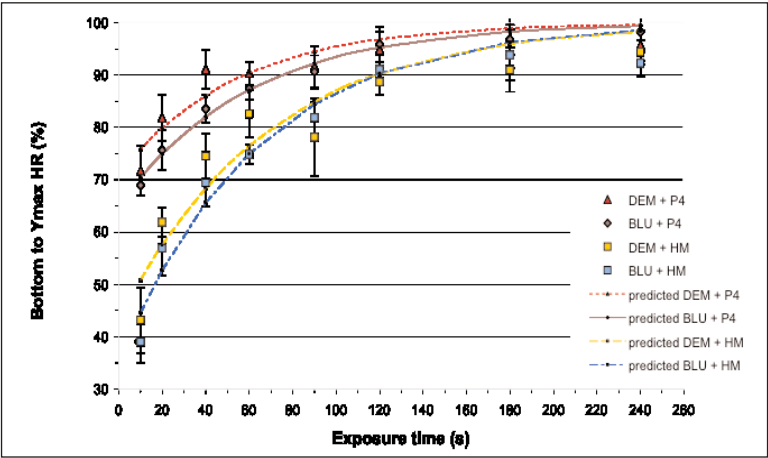


Figure 2. Hardness Ratios using  $H_{max}$  of HM & P4 cured with BLU & DEM over extended cure times.

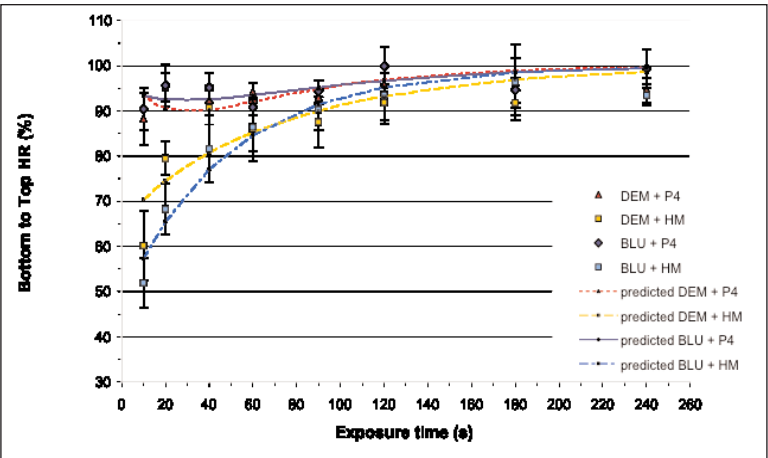


Figure 3. Per specimen B/T Hardness Ratios of HM & P4 cured with BLU & DEM over extended cure times.

The rate parameter ( $k$ ), describing how quickly maximum hardness ( $Y_{MAX}$ ) is reached, was generally higher with P4 than with HM. Values of  $k$ , as P4 ranged from 0.0498 to 0.0201, while the values of  $k$  for HM ranged from 0.0328 to 0.0135. When corresponding surface and composite were compared,  $k$ , the rate of how fast  $Y$  values approach  $Y_{MAX}$ , was always higher with the QTH light (DEM).

The exposure duration needed to achieve a bottom surface that is 80% that of  $Y_{MAX}$  ( $HR-Y_{MAX}$ ) was esti-

mated based on non-linear regression. The HM exposure interval to achieve  $HR-Y_{MAX}=80\%$  was 71 seconds for DEM and 74 seconds for BLU. Corresponding values for P4 were 21 seconds for DEM and 34 seconds for BLU (Table 3, Figure 2). In addition, per specimen bottom-to-top HRs were calculated to illustrate the result of using denominators (top-surface KH) that are  $<Y_{MAX}$  (Figure 3).

Non-linear regression of the form  $Y = (Y_{MAX} - c)(1 - e^{-kt}) + c$ , fitting top- and bottom-surface hardness scores for the respective data groups are illustrated in Figures 4 through 7. Pairwise comparisons of the LCU groups (two per composite) were used to compare the per-specimen HR, bottom KN and top KH within each cure interval (10 seconds, 20 seconds, 40 seconds, 60 seconds, 90 seconds, 120 seconds, 180 seconds and 240 seconds). For most pairwise comparisons (38 out of 48), DEM and BLU did not result in statistically different HRs or KHs within a composite group (HM or P4). Per specimen B/T hardness ratios of P4 cured with BLU & DEM were not statistically different for 10-40 seconds cure times, but per specimen B/T hardness ratios of HM cured with BLU were significantly lower than those cured with DEM for 10 to 40 seconds (Figure 3). While the hardness ratio was significantly lower, the top-surface KH of HM samples cured with BLU were significantly higher than DEM for 10 to 40 seconds (Figure 6). The percentage of bottom-surface  $H_{MAX}$  that corresponded to 0.80 of the top-surface  $H_{MAX}$  was higher with the QTH source for both HM and P4. The bottom-surface KH values of HM cured with DEM and BLU were not statistically different.

DISCUSSION

The primary intent of the current study was to illustrate the utility of using hardness measurements collected over a wide range of cure intervals in conjunction with non-linear regression to characterize the curing performance of LCUs, resin composites and LCU-composite groups. The equation was used to describe the relationship between the hardness ratio and radiant exposure ( $mJ/cm^2$ ) and predict the exposure duration required for an asymptotic value of maximum top surface hardness  $T_{MAX}$  and a  $B:T_{MAX}$  KH ratio of 0.80 for each respective curing light/composite combination.

Of the curing lights tested, Demetron Optilux 501 (DEM) represents a standard high intensity QTH LCU, and the Bluephase LED LCU is an example of a second-generation high intensity LED. Although the power and irradiance of the LED unit tested was slightly lower

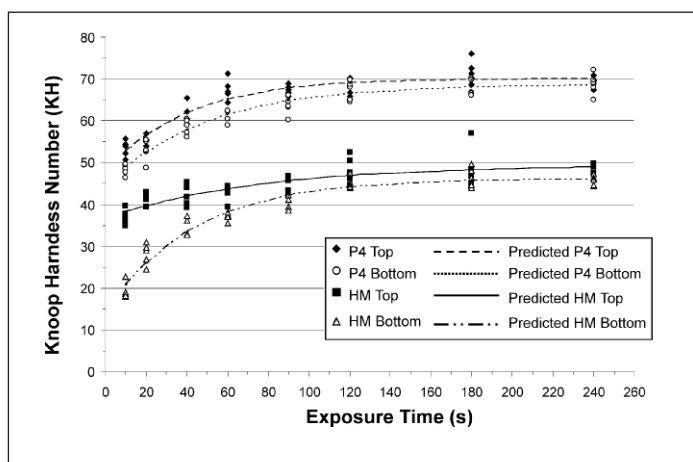


Figure 4. Top and Bottom KHS of P4 & HM cured with BLU with non-linear regression model.

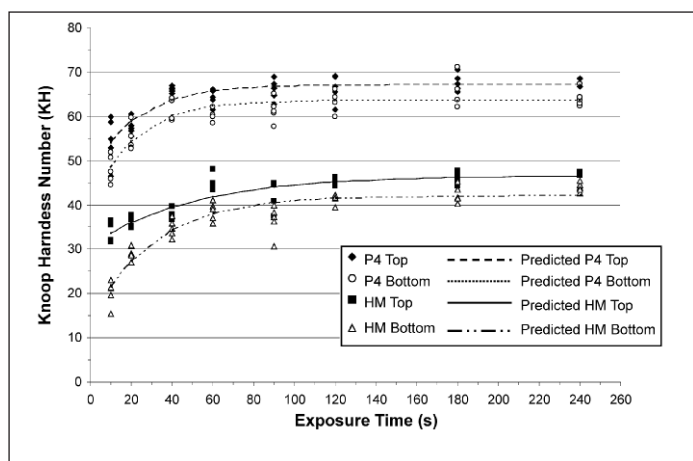


Figure 5. Top and Bottom KHS of P4 & HM cured with DEM with non-linear regression model.

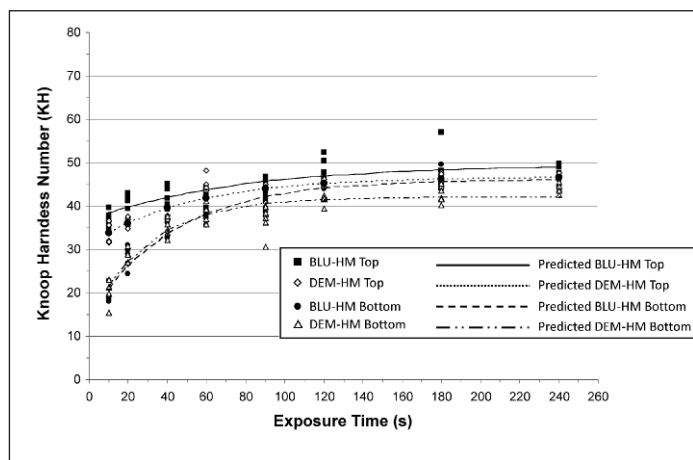


Figure 6. Top and Bottom KHS of HM cured with BLU & DEM with non-linear regression model.

than the QTH, there are now LED units available with similar or higher irradiance and power output. As power or irradiance increases, so do concerns about intrapulpal temperature increases; therefore, it is important to predict the minimal exposure duration necessary to achieve an adequate or equivalent hardness ratio based on  $H_{MAX}$ .

The current study used a maximum top hardness ( $H_{MAX}$ ) to provide a constant denominator for a microhardness ratio, which provides a more accurate assessment of sufficiency of polymerization than hardness ratios obtained on a per-specimen basis. The non-linear prediction equation:  $H = (H_{MAX} - c)(1 - e^{-kt}) + c$  was used to estimate  $H_{MAX}$  and the exposure time at which the bottom-surface hardness was 80% of  $H_{MAX}$ . Point 4 (P4) reached an  $HR-H_{MAX}$  equal to 80% with an exposure time of 21 seconds with the DEM LCU, while the BLU LCU required 34 seconds to reach this hardness criterion. The corresponding rate parameters ( $k$ ) for DEM and BLU LCUs were 0.0498 and 0.0201, respectively. HM, a microfill which is harder to cure, reached an  $HR-H_{MAX}$  equal to 80%, with exposures of 71 seconds for DEM versus 74 seconds for BLU. The corresponding rate parameters ( $k$ ) for DEM and BLU were 0.0328 and 0.0233. Both P4 and HM composites required shorter exposure times to reach 80%  $HR-H_{MAX}$  with the DEM LCU. However, the predicted  $H_{MAX}$  values for P4 and HM with DEM ( $P4=67.11$ ,  $HM=46.70$ ) were lower than the  $H_{MAX}$  values for P4 and HM when polymerized with BLU ( $P4=70.12$ ,  $HM=49.56$ ), illustrating that the rate parameter is independent of  $H_{MAX}$ .

$H_{MAX}$  a theoretical maximum obtained from the non-linear regression equation, which describes the experimentally determined KH numbers to be primarily related to the specific composite's filler loading and resin matrix, while the values of the rate parameter  $k$  are related to the LCU's absolute irradiance and the chemical constituents and photoinitiator chemistry of the composite. P4 was much easier to cure than HM in terms of exposure time needed to reach  $HR-H_{MAX}$  equal to 80% and absolute top and bottom surface  $H_{MAX}$  KH values. HM, a microfill, is generally recognized as being more difficult to cure due to the scatter of light by sub-micron ( $0.04 \mu$ ) fumed silica filler particles. Since HM required more than 70 seconds to reach  $HR-H_{MAX}$  equal to 80% with both BLU and DEM, the manufacturer's recommended 40-second cure time for HM may be inadequate to achieve optimal polymerization and physical properties. The x-axis could also be plotted as radiant exposure (exposure time x irradiance) necessary to achieve optimal polymerization.

The DEM (QTH) and BLU (LED) lights showed relatively similar performance when used with the microfill, although the time to reach  $HR-H_{MAX}$  equal to 80% was a rather lengthy 71 seconds for DEM vs 74 seconds

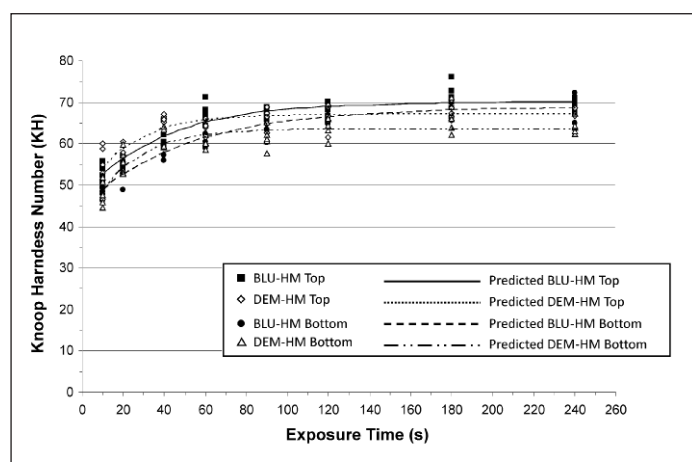


Figure 7. Top & Bottom KHs of P4 cured with BLU & DEM with non-linear regression model.

for BLU. Both exposure times are significantly longer than the manufacturer's recommended cure time of 40 seconds. One must also consider that these laboratory samples were fabricated with high irradiance lights under ideal laboratory conditions, with the distal end of the light guide in contact with the top surface of a 2.0 mm thick sample. Such conditions are rare in the clinical setting, where intervening tooth structure, matrix retainers and rubber dam clamps often increase the distance between the light guide and the bonding agent or composite, thereby rapidly decreasing radiant incidence.<sup>20</sup> It is also very difficult to limit incremental placement of a composite to 2.0 mm in a clinical setting. Any such increase in the thickness of the overlying composite further attenuates the light available to the deeper portion of the composite.<sup>21</sup> Also, the light guide was precisely centered over the sample, while intraoral alignment of the light guide with the long axis of the preparation may be impossible and, as a result, a portion of the light may be blocked by adjacent tooth structure. The hybrid composite P4 reached a  $HR-H_{MAX}$  equal to 80%, with an exposure time of 21 seconds with the DEM LCU, while the BLU LCU required 34 seconds to reach this hardness criterion. Again, while both lights reached the hardness criteria in less than 40 seconds, many clinical situations require increased exposure duration to compensate for placement situations where light attenuation is unavoidable.

Since measured irradiance of the LED and QTH LCUs was fairly similar (1,177 vs 1,379 mW/cm<sup>2</sup>), it was expected that the curing characteristics would be similar. For the majority of pairwise comparisons (38 out of 48), DEM and BLU did not result in statistically different HRs or KHs for a specific composite (HM or P4). Also, per specimen B/T hardness ratios of the hybrid P4 cured with BLU & DEM were not statistically different for 10 to 40 second cure times.

Per specimen, B/T hardness ratios of HM cured with BLU were significantly lower than those cured with DEM for 10 to 40 seconds (Figure 3). This difference in HRs could easily be misinterpreted, as the Knoop hardness numbers from the top-surface of HM samples cured with BLU were significantly higher than those obtained from samples cured with the DEM for 10 to 40 seconds (Figure 6). The bottom-surface KH values of HM cured with BLU and DEM were not statistically different. The significantly lower hardness ratios for microfill are reflected in the difference of the bottom surface rate parameter ( $k=0.0233$  and  $0.0328$ , respectively).

Although irradiance of the two lights was similar, the absolute irradiance measurement showed the QTH LCU had a wider bandwidth (389-511nm), and the higher absolute irradiance at shorter wavelengths (389-427nm) may be responsible for the differing cure characteristics. Although the relative heat output from the two units was not measured in this experiment, a higher irradiance or more power output, especially at the longer wavelength end of the bandwidth (387-511 nm), may have resulted in more heating of the composite, which can increase the degree of conversion.<sup>22</sup>

The surfaces of the samples were cured in contact with a matrix strip to enable hardness testing of the surfaces closest and farthest from the light guide without the polishing step, so as to simplify the technique. However, this may leave a resin-rich outer layer. Hardness testing conducted on this layer may not be truly representative of the bulk of the composite, and this layer is typically removed during clinical procedures. While polishing removes the resin-rich layer, it may also alter the hardness number, as the water used to avoid heating the sample (which could increase the degree of conversion) dissolves out the TEGMA, which may affect the hardness values. While the HRs were based on surfaces treated in a similar manner, these ratios should be compared to ratios obtained with polished surfaces in a future study.

One of the primary advantages of the method utilized in the current study is that the denominator ( $H_{MAX}$ ) of the ratio is constant and consistently proportional throughout the range of measurement, so that the resulting hardness ratios can be considered interval-level data. Hardness ratios obtained on a per specimen basis from a limited range of exposure durations can often result in bottom-to-top hardness ratios  $>0.80$  when top-surface KH numbers  $<H_{MAX}$  are utilized (Figure 3). The plot of per specimen hardness ratios for Point 4 in Figure 3 is relatively flat. HR values fall between 0.90 & 1.00 over a range of exposures from 10 seconds to 240 seconds, while the hardness ratios based on  $H_{MAX}$  range between 0.60 & 1.00 over the same range of exposure times. If cure time recommendations



were based on the per-specimen hardness ratios, 10 seconds or less would be deemed adequate, as all HRs exceed 0.80 and do not improve greatly with exposure times as high as 240 seconds. Figures 4 through 7 illustrate that the KH numbers in the numerator and denominator of the hardness ratio are increasing concurrently. The resulting per-specimen hardness ratio stays relatively constant over an extended range of cure times, even though the top and bottom hardness of the sample continue to improve. This is particularly true with P4, where there was very little convergence between the top and bottom surface hardness values (Figures 3-5).

As a result, the top and bottom surface hardness numbers of the shortest exposure duration resulting in a  $HR \geq 0.80$  may be significantly lower than the hardness numbers obtained with longer exposure durations, yet typically, there is only a negligible increase in the HR. As the intervals between the scale points are uneven, hardness ratios calculated on a per-specimen basis should be regarded as ordinal data. Since arithmetic operations should not be performed with ordinal data, comparisons utilizing per-specimen hardness ratios should be limited to logical operations (more than, less than, equal to). One might also consider that, prior to polymerization, the per specimen bottom-to-top surface hardness ratio, while unmeasurable, is hypothetically equal to 1.00. It is recommended that the use of any hardness ratio criteria not based on the top surface hardness =  $H_{MAX}$  be abandoned.

A further advantage of the method is the easy use of rate parameter  $k$  for comparisons of the composite, LCU and composite-LCU groups. The rate parameter  $k$ , which describes how fast  $H$  approaches  $H_{MAX}$ , demonstrated that the hybrid material cured more rapidly than the microfill irrespective of the LCU. The QTH light (DEM) reached  $H_{MAX}$  more quickly than the LED light (BLU) with both the microfill and hybrid composite. For corresponding surfaces of the same composite, the value of  $k$  for the QTH source was always greater than that of the LED source. It should be emphasized again that  $k$  is independent of  $H_{MAX}$ .

There was less of a discrepancy between the top and bottom surface  $k$  values for the microfill HM than for the hybrid P4, and this was reflected in the small difference between the times required to reach 0.80  $HR-H_{MAX}$  (71 seconds for DEM vs 74 seconds for BLU). There was a wider discrepancy between top and bottom surface  $k$  values for the QTH and LED sources with P4 composite. Accordingly, the time required to reach a  $HR-H_{MAX} = 0.80$  with the LED source took considerably longer than with the QTH source (34 seconds vs 21 seconds). There was also less disparity between  $k$  values for each light type for the top surface than for the bottom surface.

Per-specimen microhardness ratios can be easily misinterpreted and may misrepresent the relative curing performance of LCU/composite combinations being evaluated. The non-linear regression utilized to estimate cure time and hardness ratios has been shown to be superior to linear regression in describing the relationship between exposure duration required to achieve 80% bottom-surface hardness, relative to top surface  $H_{MAX}$ .<sup>18</sup> Non-linear regression analysis utilizing maximum top-surface hardness provides a more accurate method to assess the curing behavior of various resin composites (while holding the LCU constant) or to assess the curing effectiveness of various LCUs (while holding the composite constant). It is suggested that the methodology described be adopted as a more accurate indicator of adequacy of cure when evaluating various curing-light/composite combinations.

## CONCLUSIONS

Point 4 (P4) reached the criteria hardness ratio based on maximal top-surface hardness ( $HR-H_{MAX} = 80\%$ ) with exposure times of 21 seconds for DEM versus 34 seconds for BLU.

Heliomolar (HM) reached the criteria hardness ratio based on maximal top-surface hardness ( $HR-H_{MAX} = 80\%$ ), with exposures of 71 seconds for DEM versus 74 seconds for BLU.

The recommended 40-second cure time for HM may be inadequate to achieve optimal polymerization and physical properties under the curing conditions used by this study.

The relative curing behavior of different resin composites (while holding curing light constant) and the relative performance of light curing units (while holding the composite constant) can be readily assessed utilizing the described non-linear regression technique.

Separate analysis of top and bottom hardness is still necessary to avoid misinterpretation of the improved analysis using  $H_{MAX}$  and non-linear regression.

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