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Surface Microhardness of a Nanofilled Resin Composite: A Comparison of a Tungsten Halogen and a Light-Emitting Diode Light Curing Unit, *in vitro*

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Abstract - *Surface microhardness numbers (VHN) have been measured and compared for disk specimens (thickness 1.5 mm) of a commercial nanofilled resin composite cured using a range of exposure times with a quartz tungsten halogen (QTH) and light-emitting diode (LED) light-curing unit (LCU), respectively. Each LCU requires different minimum exposure times to optimise VHN with respect to the internal controls but yield bottom surface / top surface VHN ratios > 0.95 with these optimised exposure times. Both LCUs produce comparable VHNs for the top surfaces at short exposure times but the QTH LCU requires increased exposure time for comparable results with the bottom surfaces. Overall, the LCUs are capable of producing comparable VHN numbers and VHN ratios within the parameters investigated.*

KEY WORDS: Resin Composite; Nanofilled, Surface Microhardness; Light-Activation; Tungsten Halogen; Light Emitting Diode; Exposure Times

INTRODUCTION

A classification has been proposed[1] for the resin-ceramic (composite) tooth restorative materials to address the various filler types, morphologies and loadings which relate to these systems. Traditional inorganic fillers have either been of micron (ca 1-3 µ) or submicron (ca 0.05 µ) dimensions, or combinations of such fillers, to yield generic descriptors of *densified* or *microfilled*, respectively. However, a more recent development has been the introduction of systems based on nanofillers and nanotechnologies [2] such that the traditional definitions of "filler" and "resin" may be less relevant. Clearly, the corpus of clinical and laboratory test data is less extensive for these newer "nanotechnology" materials than for more traditional systems. Adequate and appropriate polymerisation is of continual interest in the setting of the resin composite materials and no less so in these novel systems to ensure that the mechanical properties of the set product are optimised. A correlation has been reported between surface microhardness of resin composite and degree of polymerisation [3, 4] such that these determinations may be a convenient and useful monitor of parameters relating to mean chain length and mean molecular mass in the polymerised system. While microhardness numbers are an indirect measurement of polymer conversion and are sensitive to small changes in polymer cross-linkages found in areas of higher conversion, the methodology is useful in that a small change in conversion may yield a large change in hardness.

Light curing units (LCU) appropriate to the setting of these systems have included quartz halogen (QTH) and the more recent solid-state light-emitting diode (LED) [5,6.] The latter are more wavelength specific to the polymerisation of resin composites based on camphoroquinone as an activator.

Attenuation of light intensity with distance from the curing-tip into the polymerising material results in reduced polymerisation [7] and a limiting depth-of-cure [8] which is related to light scattering within the material [9]**.** The use of disk specimens for testing, *in vitro*, allows the determination of bottom surface / top surface microhardness ratios for a given depth of material as an obvious monitor of "depth of cure" – published data indicating that this ratio should be in excess of 0.8 for adequate polymerisation[10]. While the clinical relevance of this value is not resolved, it would, nevertheless, appear to be a not unreasonable requirement**.**

The purpose of this investigation was to:determine the minimum exposure times consistent with: optimised surface microhardness numbers (VHN) for the top and bottom surfaces, respectively, and optimised bottom surface / top surface VHN ratios, for disk specimens (1.5 mm depth) of a nanotechnology resin composite exposed to either a QTH LCU or a LED LCU - data to be recorded at 1 hour and 24 hours post exposure. And to compare VHN data between both light curing units

MATERIAL & METHODS

The experimental procedure has been reported previously [11,12] the principal details of which were as follows: Groups of a resin composite material (Ceram X Duo, Shade DB, Lot # 0408000941, Dentsply DeTrey Gmbh, D-78467, Konstanz, Germany) were exposed in nylon washers using either a QTH LCU (Degulux Softstart, Dentsply DeTrey Gmbh, D-78467, Konstanz, Germany) at full intensity (nominally 570mW/cm^2 [13]) or a LED LCU (Smartlite IQ, Dentsply DeTrey Gmbh, D-78467, Konstanz, Germany) at full intensity

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(nominally 800 mW/cm^{2} [14]). A specimen depth of 1.5 mm was considered to be consistent with the maximum allowable for the incremental curing of resin composites[15,16] (Fig 1). Groups 1 - 6 (15 specimens per group) were exposed according to the protocols indicated (Table 1) with the light-curing tip positioned at 0.9 mm above the specimen surface (which was the thickness of the separating microscope slide). A reflective background was used under each specimen (previously used and reported in this laboratory to yield a consistent database[17]).

Top and bottom surface Vickers microhardness (VHN) numbers were recorded at 1 hour and 24 hours after the start of exposure. During the time intervals, the specimens were stored dry in an opaque box at 20°C. Group 6 acted as a control to yield optimised microhardness numbers (within the exposure parameters) - a 60 second exposure was considered to be the maximum continuous exposure time likely to be acceptable in the clinical environment. All microhardness measurements were performed using a calibrated Vickers indenter (*MVK-H1,* Mitutoyo, 1-20-1

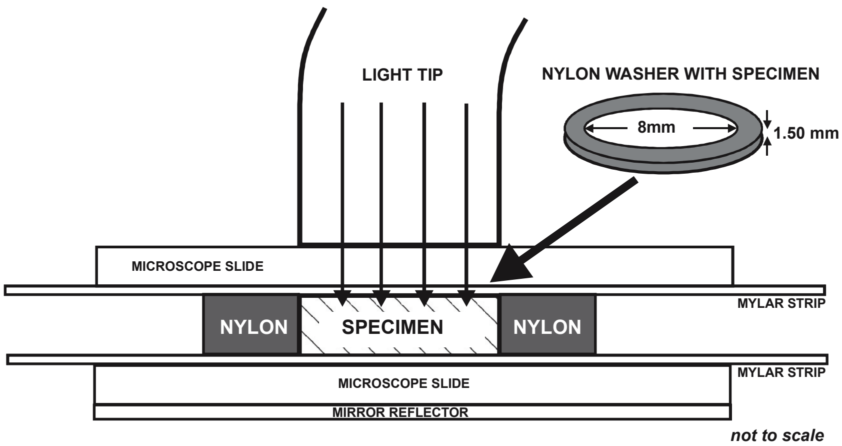

Figure 1. *Specimen preparation – a nylon washer of depth 1.5 mm is filled with resin composite and sandwiched between glass microscope slides before exposure*

Table 1. *Exposure protocols and surface microhardness numbers*

n = 15	*Group 1*	*Group 2*	*Group 3*	*Group 4*	*Group 5*	*Group 6*
EXPOSURE (s)	*5*	*10*	*20*	*30*	*40*	*60*
MEAN (SD) VICKERS MICROHARDNESS NUMBER (VHN) 1- HOUR (TOP SURFACE)						
QTH	37.9(4.1)	41.5(2.0)	43.3(1.5)	44.8(2.0)	45.8(1.4)	46.0(2.4)
LED	40.2(1.5)	40.7(1.9)	42.9(2.6)	45.4(1.5)	43.6(2.05)	43.6(1.8)
QTH - LED	-2.3	0.8	0.4	-0.5	2.2	2.4
MEAN (SD) VICKERS MICROHARDNESS NUMBER (VHN) 1- HOUR (BOTTOM SURFACE)						
QTH	23.0(5.1)	31.5(3.2)	39.4(3.0)	42.1(2.1)	43.7(1.7)	44.5(2.1)
LED	29.4(4.2)	35.5(4.4)	42.4(2.4)	44.3(2.8)	43.6(2.1)	43.3(1.7)
QTH - LED	-6.4	-4.0	-2.9	-2.2	0.1	1.2
HARDNESS RATIO QTH	0.60	0.76	0.91	0.94	0.95	0.97
(BOTTOM/TOP)	[0.53,0.68]*	[0.71,0.81]	[0.87,0.95]	[0.91,0.97]	[0.93,0.97]	[0.96,0.98]
HARDNESS RATIO LED	0.73	0.86	0.99	0.98	1.0	0.99
(BOTTOM/TOP)	[0.66,0.79]	[0.81,0.92]	[0.96,1.02]	[0.94,1.01]	[0.96,1.04]	[0.96,1.02]
MEAN (SD) VICKERS MICROHARDNESS NUMBER (VHN) 24- HOURS (TOP SURFACE)						
QTH	46.8(3.8)	46.8(3.7)	52.5(2.1)	53.2(2.0)	53.9(2.9)	54.9(2.8)
LED	48.8(2.4)	47.7(3.5)	53.1(2.1)	52.7(2.5)	51.4 (2.2)	52.8(3.0)
QTH - LED	-1.9	-0.8	-0.6	0.5	2.5	2.2
MEAN (SD) VICKERS MICROHARDNESS NUMBER (VHN) 24- HOURS (BOTTOM SURFACE)						
QTH	26.6(5.8)	34.2(4.6)	46.4(2.2)	49.6(2.0)	52.0(2.4)	53.7(3.1)
LED	34.4(4.3)	42.2(5.8)	51.7(2.0)	52.3(4.1)	51.3(2.1)	52.0(2.5)
QTH - LED	-7.8	-8.0	-5.3	-2.7	0.7	1.7
HARDNESS RATIO QTH	0.56	0.73	0.88	0.93	0.96	0.98
(BOTTOM/TOP)	[0.49,0.63]	[0.67,0.78]	[0.85,0.91]	[0.90,0.97]	[0.92,1.01]	[0.95,1.01]
HARDNESS RATIO	0.70	0.88	0.97	0.99	1.0	0.99
LED (BOTTOM/TOP)	[0.65,0.75]	[0.82,0.94]	[0.95,1.00]	[0.94,1.05]	[0.97,1.03]	[0.94,1.03]

** 95% confidence intervals*

Sakato, Takatsu-Ku, Kawasaki-Shi 213, Japan) using a load of 300g and a dwell time of 10 seconds.

Statistical analysis was carried out using SPSS for Windows (Version 12). A significance level of 5% was used for all statistical tests. A repeated measures analysis of variance was used to investigate the significance of the within-specimen factors – elapsed time (1 hour and 24 hours) and position (top, bottom). The between-specimen factor was the experimental group (groups 1 - 6) and LCU (QTH and LED). When summarising ratios (bottom/top) of microhardness measurements, the ratios were transformed to the log scale. The mean, standard deviation and confidence intervals for the mean were obtained using the log scale. Obtaining the antilog of the mean of the logged data yielded the geometric mean. The standard deviation of the logged data cannot be meaningfully back transformed so instead a 95% confidence interval for the geometric mean is included in Table 1. Post-hoc tests were used to test for differences between the levels of a factor.

Ceram-X duo is a combined densified – nanofilled material. The filler is a combination of conventional glass particles (diameter 1 μ approx) with nanoscale polysiloxane clusters (diameter 10 nm approx). The resin phase is a further polysiloxane material derived from nanoscale monomer entities (diameter 2-3 nm, approx). Total filler content (glass & nanofiller) is 57% (vol), 76% (mass).

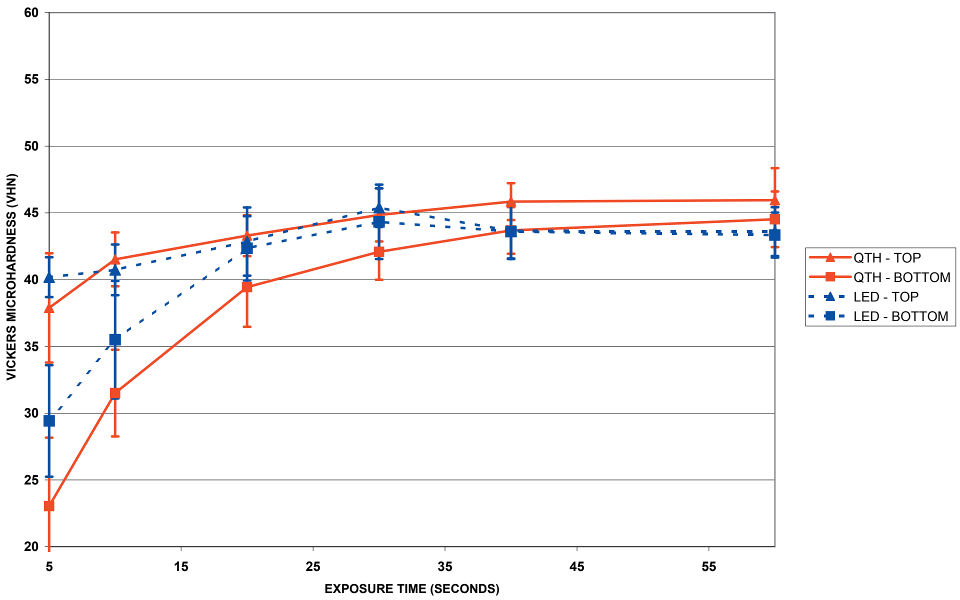

Figure 2. *Mean surface microhardness (VHN) for a resin composite exposed to a quartz halogen and a LED light curing unit (1-hour)*

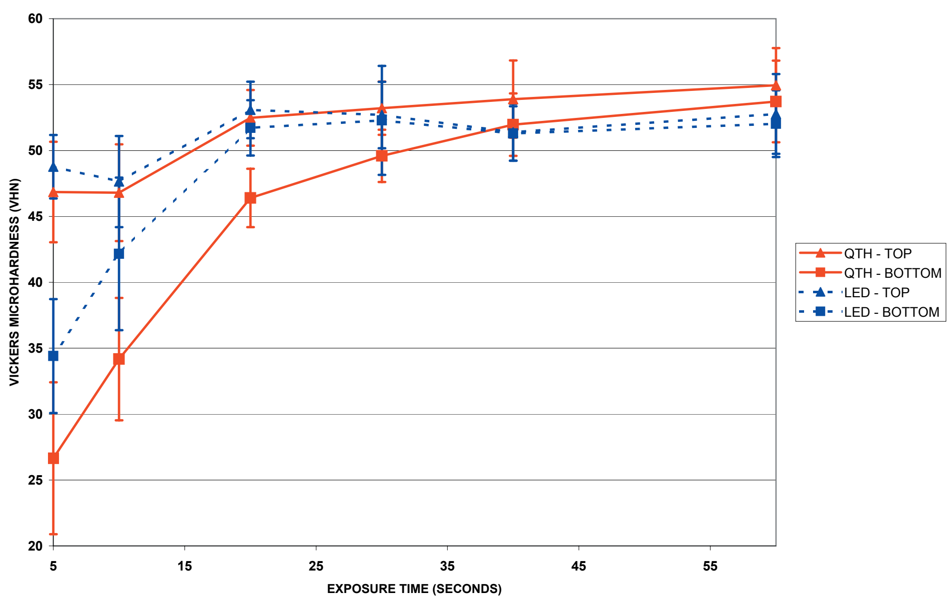

Figure 3. *Mean surface microhardness (VHN) for a resin composite exposed to a quartz halogen and a LED light curing unit (24-hour)*

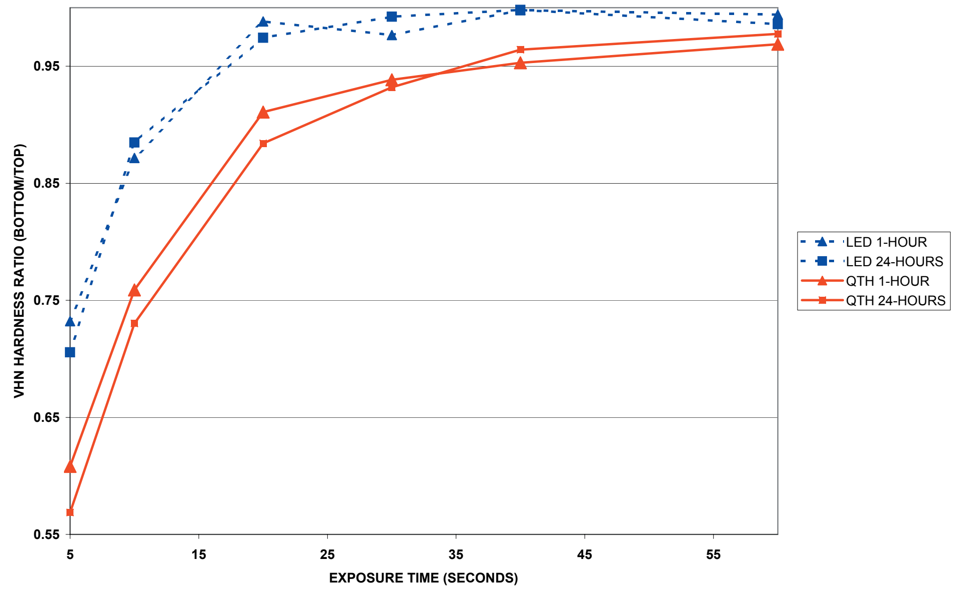

Figure 4. *Microhardness ratios (VHN bottom/top) for a resin composite exposed to a quartz halogen and a LED light curing unit*

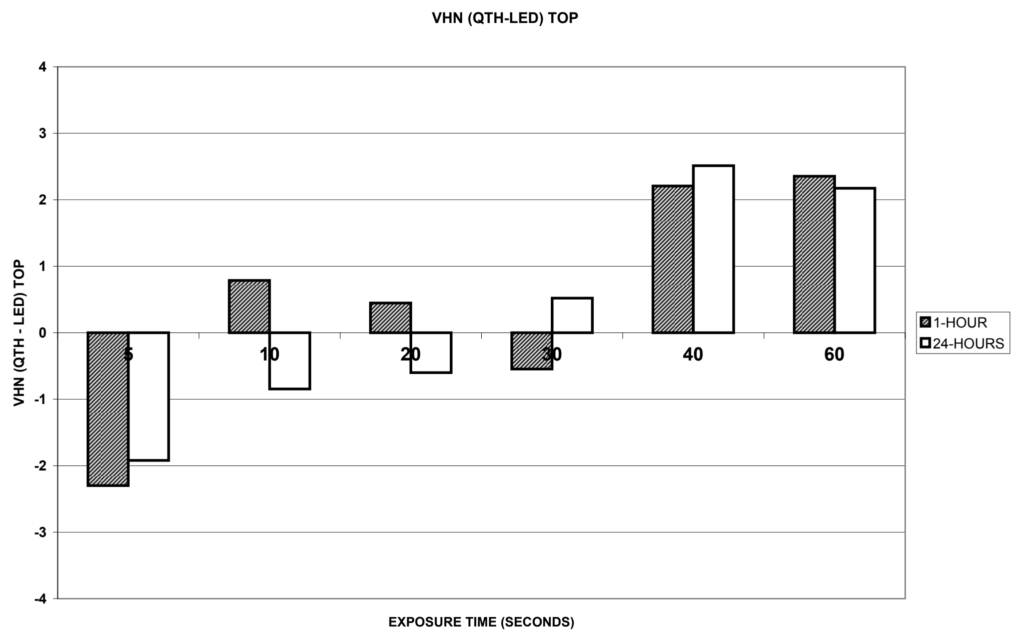

Figure 5. *Mean difference in microhardness for a resin composite exposed to two light-curing units (QTH – LED), top surface*

RESULTS

VHN data are presented in Table 1 and in Figs 2-6. The results of selected statistical analyses are presented in Table 2 (for descriptive purposes only to demonstrate the patterns of differences across groups and lamps. 96 comparisons were carried out and a standard Bonferroni adjustment for multiple comparisons (dividing the significance level of 5% by the number of tests carried out) would result in a new significance level of 0.05%. None of the differences in Table 2 are statistically significant using a 0.05% level of significance. Results, which are statistically significant at the 5% significance level, are in bold.).

For the QTH LCU, an exposure of 30 seconds, within the range of exposures investigated, was sufficient to maximise the top surface VHN data with respect to the control, at both 1-hour and 24-hour elapsed times; the corresponding data for the bottom surface being 40 seconds. The bottom surface / top surface VHN ratio had optimised at 40 seconds exposure. The corresponding data (top, bottom & ratio) for the LED LCU were 20 seconds exposure with the exception of one unexpected datum.

For most exposure times (groups 1- 4) there are no significant differences between the two LCUs relating to top surface VHN data (1-hour and 24-hours) – and these similarities are also manifest in the small differences between the VHN data (Fig 5). The analyses suggest differences between both data at 40 seconds exposure (group 5) and one datum for 60 seconds (group 6 – 1-hour) which relates to an unexpected reduction in VHN for the LED lamp for these exposure times. This may indicated that such long exposure times are not appropriate to the operation of this unit. But, for reason-

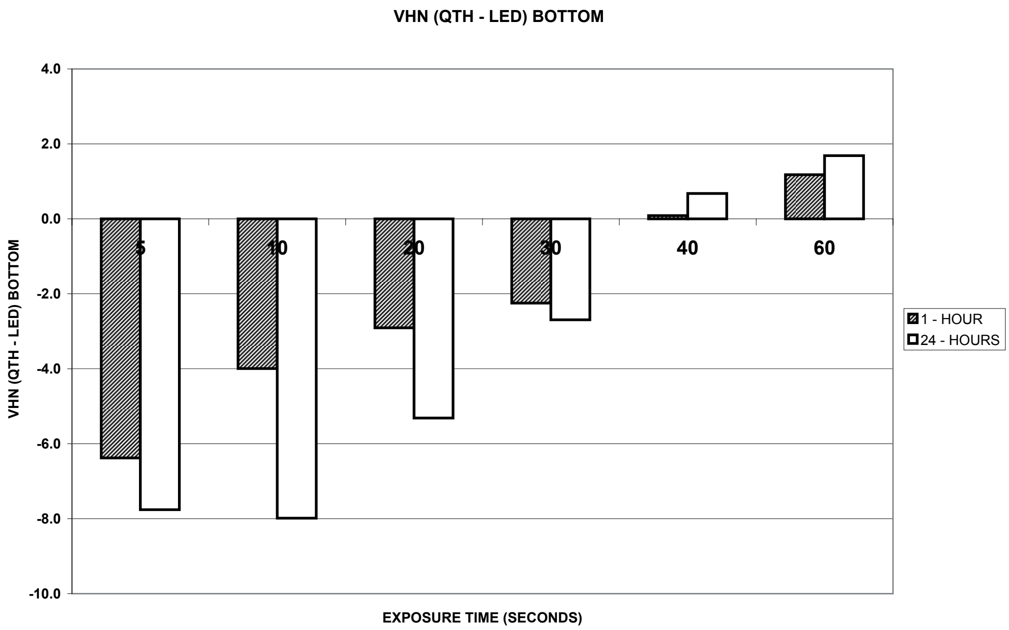

Figure 6. *Mean difference in microhardness for a resin composite exposed to two light-curing units (QTH – LED), bottom surface*

able exposure times (up to 30 seconds), it is clear that both lamps will cure the top surface equally well.

There was a significant difference ($p < 0.001$) over time (1 hour and 24 hours) for readings taken at the top and readings taken at the bottom, respectively. As well as a significant difference ($p < 0.001$) across location (top and bottom) for readings taken at 1 hour and 24 hours.

There was no significant difference between the bottom surface / top surface VHN ratios within each group over time.

DISCUSSION

The reduced exposure times required to optimise the VHN's (top & bottom) and VHN ratio, for the LED LCU, compared with the QTH LCU, are probably consistent with increased polymerisation efficiency in this unit, in terms of increased degree of polymerisation, most likely relating both to the increased nominal irradiance and, possibly, a more appropriate spectral distribution of the delivered wavelengths. In this regard, the emission spectrum of the LED lamp can be "tuned" in manufacturing to a narrow wavelength range (depending on semiconductor composition) and may suit the activator chemistry (eg camphoroquinone).

These effects have clear implications with respect to clinical time management, in that the LED LCU will attain optimal VHN data, with respect to this unit, at correspondingly reduced exposure times. This has particular significance in the overall time taken for incremental curing of deeper layered restorations.

It is clear that both LCUs will produce comparable VHN bottom/top ratios given sufficient exposure time and elapsed time after exposure (Table 2). These data are considerably in excess of the value of 0.80 (for the optimised exposure times) considered to reflect an adequate degree of polymerisation[10].

The generalised outcome from the comparison of LCUs is that both units will yield similar top surface VHN data even for relatively short exposure times. However, correspondingly longer exposure times are required in the case of the QTH LCU to yield similar results to the LED unit for bottom surfaces with a 1.5 mm depth.

The effects of exposure time and elapsed time after exposure on VHN are broadly comparable to data reported from this laboratory [11,12] on the curing of a conventional resin composite. The effect of elapsed time on the development of surface microhardness is of particular interest with regard to two aspects – the significant increase in all corresponding values from 1-hour to 24-hours for both LCUs and the lack of an increase in corresponding microhardness ratios over this period. These observations indicate that polymerisation continues during this period within the bulk of the material but, because of the time independent nature of the bottom:top hardness ratios, a disproportionate increase in hardening does not occur at the bottom surface.

It is of interest to compare these results with a previously-reported study [17] relating to two LCUs using a similar experimental design (1.5 mm depth) and a conventional densified resin composite. In contrast to the present data, VHN numbers for the LED unit were significantly less, at shorter exposure times, for both top and bottom surfaces (elapsed times of 1-hour and 24-hours, respectively) when compared with the QTH unit. This is undoubtedly a reflection of the reduced irradiance of this previous LED unit when compared with the LED device used in this current work (259.2 mW/cm^2, "First Generation"; 800 mW/cm^2 "Second Generation") and underlines the importance of the selection of an LED unit of adequate power.

Future work will address a rigorous comparison of these VHN data with those for the previously-referenced densified composite[17]. In addition, the question is raised of whether nanofilled materials are comparable to traditional microfilled materials in physical and mechanical properties[18]. In this respect, a comparison of VHN data will be of interest in further protocols.

Table 2. *Selected statistical analyses data*

GROUP		*QTH COMPARISON WITH QTH CONTROL*	*LED COMPARISON WITH LED CONTROL*	*QTH vrs LED*
1	TOP – 1hr	**<0.005**	**<0.05**	0.056
	TOP – 24hr	**<0.05**	**<0.003**	0.11
	BOTTOM –1hr	**<0.001**	**<0.001**	**0.001**
	BOTTOM – 24hr	**<0.005**	**<0.001**	**<0.001**
	RATIO – 1hr	**<0.05**	**<0.001**	**0.01**
	RATIO – 24hr	**<0.005**	**<0.001**	**0.001**
2	TOP – 1hr	**<0.005**	**<0.05**	0.28
	TOP – 24hr	**<0.05**	**<0.004**	0.52
	BOTTOM –1hr	**<0.001**	**<0.001**	**0.009**
	BOTTOM – 24hr	**<0.005**	**<0.001**	**<0.001**
	RATIO – 1hr	**<0.05**	**<0.004**	**0.003**
	RATIO – 24hr	**<0.005**	**<0.05**	**<0.001**
3	TOP – 1hr	**<0.005**	0.37	0.57
	TOP – 24hr	**<0.05**	0.75	0.45
	BOTTOM –1hr	**<0.001**	0.20	**0.006**
	BOTTOM – 24hr	**<0.005**	0.71	**<0.001**
	RATIO – 1hr	**<0.05**	0.74	**0.001**
	RATIO – 24hr	**<0.05**	0.56	**<0.001**
4	TOP – 1hr	0.18	**0.006**	0.40
	TOP – 24hr	0.06	0.94	0.54
	BOTTOM –1hr	**<0.001**	0.25	**0.02**
	BOTTOM – 24hr	**<0.005**	0.84	**0.03**
	RATIO – 1hr	0.08	0.36	0.10
	RATIO – 24hr	0.05	0.89	**0.04**
5	TOP – 1hr	0.88	0.96	**0.002**
	TOP – 24hr	0.33	0.16	**0.01**
	BOTTOM –1hr	0.25	0.77	0.84
	BOTTOM – 24hr	0.09	0.39	0.41
	RATIO – 1hr	0.14	0.80	**0.03**
	RATIO – 24hr	0.65	0.72	0.21
6	TOP – 1hr	**QTH control**	**LED control**	**0.005**
	TOP – 24hr	**QTH control**	**LED control**	0.051
	BOTTOM –1hr	**QTH control**	**LED control**	0.10
	BOTTOM – 24hr	**QTH control**	**LED control**	0.11
	RATIO – 1hr	**QTH control**	**LED control**	**0.03**
	RATIO – 24hr	**QTH control**	**LED control**	0.67

CONCLUSIONS

Observations relate to a 1.5 mm depth.

QTH LCU (elapsed times of 1-hour and 24-hours, respectively) - requires 30 seconds exposure to optimise top surface VHN data with respect to the control; 40 seconds for bottom surfaces and for the bottom / top VHN ratio. LED LCU (elapsed times of 1-hour and 24-hours, respectively) - generally requires 20 seconds exposure to optimise both surfaces and the VHN ratio with respect to the controls. QTH & LED LCUs - both produce VHN ratios > 0.95 for the optimal exposure times.

QTH vrs LED LCUs (elapsed times of 1-hour and 24-hours, respectively) - both LCUs produce comparable VHNs for the top surfaces at short exposure times – the QTH LCU requires increased exposure time for comparable results with the bottom surfaces.

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