©Operative Dentistry, 2011, **36-1**, 98-103

Effect of Reduced Exposure Times on the Microhardness of Nanocomposites Polymerized by QTH and Second-generation LED Curing Lights

SM Marchan • D White • WA Smith
V Raman • L Coldero • V Dhuru

Clinical Relevance

Reduced polymerization times suggested with newer generation LED-curing lights may not be suitable to ensure sufficient conversion of all types of nanocomposites at depths of 2 mm.

*Shivaughn M Marchan, DDS, The University of the West Indies, Unit of Restorative Dentistry, School of Dentistry, Eric Williams Medical Sciences Complex, Trinidad and Tobago, West Indies

Daniel White, BSc, PhD, The University of Trinidad and Tobago, Point Lisas Campus, Trinidad and Tobago, West Indies

William A Smith, DDS, MSc, MBA, The University of the West Indies, School of Dentistry, Unit of Restorative Dentistry, Eric Williams Medical Sciences Complex, Trinidad and Tobago, West Indies

Vidya Raman, DDS, The University of the West Indies, School of Dentistry, Unit of Restorative Dentistry, Eric Williams Medical Sciences Complex, Trinidad and Tobago, West Indies

Larry Coldero, DDS, MSc, The University of the West Indies, School of Dentistry, Unit of Restorative Dentistry, Eric Williams Medical Sciences Complex, Trinidad and Tobago, West Indies

Viendra Dhuru, DDS, MSc, PhD, Marquette University School of Dentistry, Department of General Dental Sciences, (Dental Materials and Operative Dentistry), Milwaukee, WI, USA

*Reprint request: Champs Fleurs, 12345, Trinidad and Tobago, West Indies; e-mail: shivaughn.marchan@sta.uwi.edu

DOI: 10.2341/08-093-LR2

ABSTRACT

This study investigated the effectiveness of polymerization of various curing regimes on five nanocomposite restorative materials—Z350, Grandio, Clearfil Majesty Esthetic, Ice and Tetric EvoCeram—by utilizing microhardness measurements. Five (n=5) disc-shaped specimens of each material were subjected to one of three curing regimes: curing with a halogen light for 20 seconds, curing with an LED light for 20 seconds and curing with an LED light for 10 seconds. Immediately following curing, hardness measurements were made with a Vickers indenter at

five different locations on both the top and bottom surfaces of each disc. The mean for each surface was calculated. Data were analyzed using a one-way ANOVA and post-hoc Tukey HSD (α=0.05). The results demonstrated that among the Z350 composite samples, top and bottom microhardness values showed no statistical differences when cured with the halogen 20 second or LED 20 second regimes (p>0.05). Comparison of the top and bottom values of discs cured with the LED 10 second regime demonstrated significant differences (p<0.0001). Grandio samples cured with the halogen 20 second regime showed no statistical differences between top and bottom microhardness values (p>0.05); however, the bottom values of Grandio discs cured with the LED 20 second and 10 second regimes were significantly lower when compared with top surface values (p=0.001 and p<0.0001, respectively). Clearfil Majesty Esthetic, Ice and Tetric EvoCeram samples cured with the halogen 20 second regime produced significantly lower bottom microhardness values, while both LED regimes produced top and bottom surfaces that were statistically comparable. The conclusion may be drawn that LED 10 second curing regimes were insufficient to cure Z350 and Grandio, while they were adequate for curing Clearfil Majesty Esthetic, Ice and Tetric EvoCeram.

INTRODUCTION

Dental composites have conventionally been polymerized with quartz-tungsten-halogen (QTH) light-curing units (LCUs). Recently, newer curing units with various irradiation modes have been introduced to the profession. These include lasers, plasma arc and light-emitting diodes (LEDs). Even though these newer irradiation sources vary in properties, such as intensity, exposure time and wavelength spectrum, the aim of most units is to decrease curing time and reduce polymerization shrinkage, along with the associated stresses, and increase the degree of conversion of resin.[1-3]

LED units produce light within a very narrow wavelength spectrum that falls within the absorption spectrum of camphoroquinone, a commonly employed photoinitiator in dental composite systems.[4] This property makes these units far more efficient; however, research has demonstrated that composites cured with earlier versions of these light sources have inferior mechanical properties, such as microhardness or compressive strength when compared to composites cured with quartz-tungsten-halogen lights.[5]

Second-generation LED lights, such as the Elipar Freelight 2, are purported by the manufacturer to achieve a 50% reduction in cure time due to an increased light intensity. According to the manufacturer's information, Freelight 2 uses a larger semiconductor crystal compared to conventional LED lights. This kind of crystal increases both the illuminated area and light intensity.

The physical and mechanical properties of dental composites are determined primarily by the filler content, particle size and particle size distribution.[6] Researchers, however, have demonstrated that the resin matrix also plays an important role in influencing the mechanical properties of composite materials, such as flexural strength.[7-8] The degree of conversion of the resin matrix and, accordingly, the dental composite's physical properties, are dependent on radiation exposure, which is the product of irradiance value and irradiation time delivered during the polymerization process.[9-10]

Hardness or microhardness is often traditionally used as an indirect measurement of effectiveness of composite cure or the degree of conversion.[11-12] Microhardness measurements, though, are affected not only by the degree of resin conversion, but by the type and volume percentage of filler, storage conditions and the presence or absence of an oxygen-inhibited layer.[6,12-13] Using hardness measurements alone to measure the degree of conversion may be problematic. Some researchers have noted a predictable relationship between degree of conversion and the ratio of hardness measured at the bottom and top surfaces of beam-shaped specimens.[14] However, other studies have shown no strong correlation between hardness and the degree of conversion.[6]

The aim of the current study is to quantify the effect, if any, that differing irradiation sources (halogen and second-generation LED) may have on one nanofilled and four nanohybrid tooth-colored composite restorative materials by measuring their microhardness values.

METHODS AND MATERIALS

Five composites materials: one nanofilled (Z350 [3M ESPE, St Paul, MN, USA]) and four nanohybrids, (Grandio [Voco, Cuxhaven, Germany], Clearfil Majesty [Kuraray America Inc, New York, NY], Ice [SDI, Bayswater, Victoria, Australia] and Tetric EvoCeram [Ivoclar Vivadent, Schaan, Liechtenstein]) of shade A3 were utilized for this study. The curing lights used were the 3M Elipar Freelight LED light (3M ESPE) and the Biolite 2100 halogen light (Medeco International, Inc, Miami, FL, USA). Prior to and during preparation of the composite samples, the output of both lights was measured with radiometers (Demetron LED and Halogen radiometers, Kerr Corporation, Orange, CA, USA), the results of which are presented in Table 1.

All the resin composite specimens for mechanical testing were exposed to one of three curing regimes: (a) curing according to the manufacturer's instructions with the halogen light (20 seconds); (b) curing according to the manufacturer's instructions with the LED light (20 seconds) and (c) curing at half of the manufacturer's recommended curing time with the LED light (10 seconds).

Five specimens of each composite were fabricated for each light-curing regime. Disc-shaped specimens were prepared for hardness testing by curing the composites in 2 mm x 8 mm split brass molds, with the upper and lower surfaces covered with Mylar strips to ensure smooth surfaces and prevent formation of an oxygen inhibited layer. The tips of the light-curing units were placed in direct contact with the Mylar strips during curing. Immediately following curing, the specimen was mounted on a hardness tester (Micromet 2130 Microhardness Tester, Buehler, Lake Bluff, IL, USA) to assess the Vickers hardness number (VHN). A 500 g load was applied through a diamond indenter for 15 seconds. Five readings equally distributed over the surface, but well away from the periphery of the sample, were taken for both the top and bottom of each specimen and the mean calculated for each surface for that particular specimen. The group mean was then calculated for the five specimens. The specimens were assumed to have been selected from a normal population, with equal variances, as demonstrated by use of the homogeneity-of-variance Levene's test.

Data were evaluated with a one-way Analysis of Variance (ANOVA) followed by a post-hoc Tukey HSD (alpha=0.05).

RESULTS

The VHN data are shown in Table 2. Analysis of the variance of the means (ANOVA) showed significant differences ($p<0.05$) among the values of the tested groups. For each composite group and subset of the curing regime, the means of the top and bottom values were compared. Additionally, each composite's surface value was compared to analogous surfaces in the same group, thus comparing the efficiency of the depth of cure of the various curing regimes across that particular composite group.

Generally, the Grandio specimens showed the highest hardness values when compared with the other tested composites.

In the Z350 group, there was no significant difference between the top and bottom VHN values when cured with the halogen 20 second ($p=1.00$) and LED 20 second ($p=0.669$) curing regimes. When Z350 was cured with the LED 10 second regime, however, the bottom values were significantly lower compared to the top values ($p<0.0001$). Comparison of the

Table 1: *Radiation Energy Output of the Curing Lights Used*

Light Curing Units	Biolite 2100 Quartz-Tungsten-Halogen (Halogen)	495 mW/cm²
	Elipar FreeLight-2 Light Emitting Diode (LED)	890 mW/cm²

Table 2: *Mean (standard deviation) Vickers Microhardness Values for the Five Resin Composites Cured by Various Regimes*

Material	Light Curing Regime	Top VHN	Bottom VHN
Z350	Biolite (20 seconds)	65.0 (1.6)	64.3 (2.6)
	Elipar (20 seconds)	61.8 (1.4)	59.4 (1.7)
	Elipar (10 seconds)	64.1 (1.7)	54.6 (2.5)*
Grandio	Biolite (20 seconds)	73.7 (1.8)	70.0 (1.8)
	Elipar (20 seconds)	75.4 (1.7)	70.0 (1.8)*
	Elipar (10 seconds)	72.0 (0.1)	66.3 (1.5)*
Clearfil Majesty	Biolite (20 seconds)	33.3 (0.4)	26.8 (0.8)
	Elipar (20 seconds)	27.5 (0.8)	26.9 (0.7)
	Elipar (10 seconds)	28.9 (1.2)	26.0 (0.6)
Ice	Biolite (20 seconds)	51.4 (6.0)	43.0 (3.8)*
	Elipar (20 seconds)	51.5 (3.2)	45.6 (2.7)
	Elipar (10 seconds)	47.3 (3.0)	43.6 (2.1)
Tetric EvoCeram	Biolite (20 seconds)	34.7 (2.1)	28.8 (2.6)*
	Elipar (20 seconds)	33.6 (1.4)	33.8 (1.2)
	Elipar (10 seconds)	30.7 (1.8)	30.1 (1.7)

*(*denotes statistical differences between the top and bottom microhardness values)*

top VHN values across the Z350 group revealed no statistically significant differences when cured with the various curing regimes ($p>0.05$). Conversely, comparison of the bottom values across the Z350 group revealed significant differences among the three regimes (halogen 20 seconds vs LED 20 seconds [$p=0.005$), halogen 20 seconds vs LED 10 seconds [$p<0.0001$], LED 20 seconds vs LED 10 seconds [$p=0.006$]).

In the Grandio group, there was a significant difference between the top and bottom microhardness values when cured with the LED curing regimes only (LED 20 seconds [$p=0.001$], LED 10 seconds [$p<0.0001$]). When comparing top values across the Grandio specimens, there was no significant difference when cured with the three different regimes. A comparison of the bottom values across the Grandio grouping revealed no difference between the halogen 20 second and LED 20 second regimes; however, there was a significant difference between these two curing regimes and that of the LED 10 second curing regimes ($p<0.0001$).

With the Clearfil Majesty group, there was a significant difference between the top and bottom values when cured with the halogen 20 second ($p=0.002$) regime. Comparing the top surfaces across this group revealed significant differences in hardness between specimens cured with the halogen 20 second and LED 20 second regimes (halogen 20 seconds vs LED 20 seconds [$p=0.017$]).

When comparing the Ice specimens, there were significant differences between the top and bottom values with the halogen 20 second ($p<0.0001$) and LED 20 second ($p=0.016$) regimens. Across this group, there were no significant differences when comparing analogous top or bottom surfaces.

The Tetric group produced significant differences in top and bottom values with only the halogen 20 second regime ($p<0.0001$). Across the group, there were no significant differences in analogous top or bottom surfaces.

DISCUSSION

The current study evaluated the effect of the Elipar Freelight 2 LED LCU and a conventional halogen LCU, Biolite 2100, on the efficiency of curing five nanocomposite materials by using the indirect physical measurement of microhardness. There is a high correlation between hardness and degree of conversion.[15] It was also stated that, at higher levels of conversion, hardness is more sensitive than spectroscopic methods of measurement.[16] The main drawback of using this measurement, though, is that microhardness is a compound measure of both resin matrix and fillers. Despite this drawback, the indirect method of employing microhardness testing as an indicator of completeness of polymerization is widely used and accepted.[17-18]

Since microhardness measurements are impacted by the cured resin matrix, filler type and filler loading, and not necessarily resin conversion alone, this may explain the overall differences in the microhardness values of all the tested composites. There was a general trend for the nanohybrid composites, except for Grandio, to have lower hardness values. These finding are consistent with those of de Moraes and others.[19] With Grandio having a filler loading of 71.4% (by volume), the highest of all the composites tested produced the highest overall microhardness values. The results bear with the statement that resin composites with higher filler content yield higher hardness values.[20]

It appears that, at 2 mm increments, Z350 composite can be sufficiently cured with either the halogen 20 second or LED 20 second regimes; however, at 10 seconds, not enough conversion of the resin occurred to have hardness values comparable to top values. This could be explained by the fact that the resin matrix of Z350 is composed mainly of urethane dimethracylate (UDMA) and Bisphenol-A polyethylene gycol diether dimethracylate (BIS-EMA), which are high viscosity resins.[21] Such resins show lower conversion rates because of limited mobility of free radicals at lower degrees of polymerization.[22]

Additionally, curing for 10 seconds with the LED light would possibly not be sufficient for adequate free radicals activation with associated curing through the entire thickness of the sample. Indeed, Hasler and others,[23] in a study of the degree of polymerization in deep cavities using microhardness measurements, concluded that the degree of polymerization was strongly influenced by polymerization time.

Among the Z350 samples, only the halogen 20 second regime seemed to cause significant overall conversion on the bottom surfaces. This apparent discrepancy between the 20 second halogen and 20 second LED curing regime could possibly be explained by the amount of light penetration of the narrow wavelength spectrum of the LED light, as curing through the Z350 sample occurred. This decrease in penetration may be less for halogen LCUs, since these units have higher outputs for the longer wavelengths of light produced.[24]

Across the Grandio grouping, the inadequacy of the LED regimes to sufficiently cure the bottom of the samples may possibly be attributed to an even greater amount of light degradation due to the higher filler loading of this composite, causing even less penetration of light through the entire thickness of the specimen.

With the latter three composite groups tested, that is, Clearfil Majesty Esthetic, Ice and Tetric EvoCeram, the trend of the halogen 20 second regime to produce lower bottom hardness values was surprising. Also surprising was the apparent ability of both LED regimes to produce microhardness values that were statistically comparable on the top and bottom surfaces of these three tested composites. Perhaps the interaction of various filler particle sizes in nanohybrid materials works in concert to affect light transmittance properties through the thickness of the sample, which is not yet thoroughly understood.

It should be noted that the actual hardness values of the resin composites achieved in clinical situations would be smaller than those achieved in the current study, and they would depend upon the distance between the tip of the curing light and the top of the restoration, as well as the shade of the restorative material. Clinically, it would be rarely possible to place the light tip directly in contact with the restorative material, and the darker shades of material would need longer exposure times.

CONCLUSIONS

Within the limitations of this study, the following conclusions may be drawn:

1) The nanocomposite restorative Grandio has higher overall microhardness values compared to the other tested composites.
2) Ten second curing regimes with the Elipar LED Freelight 2 were unable to adequately cure to a depth of 2 mm for the materials Z350 and Grandio.
3) Grandio, when cured with the LED light, required longer curing times to achieve maximum microhardness measurements.
4) The nanohybrids tested: Clearfil Majesty Esthetic, Ice and Tetric EvoCeram (with the exception of Grandio), generally produced lower microhardness values compared to the nanofilled composite Z350.
5) Clearfil Majesty Esthetic, Ice and Tetric EvoCeram, when cured with the Elipar LED 10 second regime, appeared to produce adequate bottom microhardness values.

(Accepted 11 August 2010)

References

1. Yap AU, Soh MS & Siow KS (2002) Effectiveness of composite cure with pulse activation and soft-start polymerization *Operative Dentistry* **27(1)** 44-49.
2. Peutzfeldt A, Sahafi A & Asmussen E (2000) Characterization of resin composites polymerized with plasma arc curing units *Dental Materials* **16(5)** 330-382.
3. Sakaguchi RL, Sasik CT, Bunczak MA & Douglas WH (1991) Strain gauge method for measuring polymerization contraction of resin composite restoratives *Journal of Dentistry* **19(5)** 312-316.
4. Felix CA, Price RBT & Andreou P (2006) Effect of reduced exposure times on the microhardness of 10 composites cured by high power LED and QTH curing lights *Journal of the Canadian Dental Association* **72(2)** 147a-147g.
5. Jandt KD, Mills RW, Blackwell GB & Ashworth SH (2000) Depth of cure and compressive strength of dental composites cured with blue light emitting diodes (LEDs) *Dental Materials* **16(1)** 41-47.
6. Chung KH & Greener EH (1990) Correlation between degree of conversion filler concentration and mechanical properties of posterior composite resins *Journal of Oral Rehabilitation* **17(5)** 487-494.
7. Kawaguchi M, Fukushima & Horibe T (1989) Effect of monomer structure on the mechanical properties of light cured composite resins *Dental Materials Journal* **8(1)** 40-45.
8. Peutzfeld A (1997) Resin composites in dentistry: The monomer systems *European Journal of Oral Sciences* **105(2)** 97-116.
9. Halvorson RH, Erickson RL & Davidson CL (2002) Energy dependent polymerization of resin-based composite *Dental Materials* **18(6)** 463-469.
10. Emami N & Soderholm KJ (2003) How light irradiance and curing time affects monomer conversion in light cured resin composites *European Journal of Oral Sciences* **111(6)** 536-542.
11. Neo BJ, Soh MS, Teo JW & Yap AUJ (2005) Effectiveness of composite cure associated with different light-curing regimes *Operative Dentistry* **30(6)** 671-675.
12. Besnault C, Pradelle-Plasse N, Picard B & Coon P (2003) Effect of a LED versus halogen light cure polymerization on the curing characteristics of three composite resins *American Journal of Dentistry* **16(5)** 323-328.
13. Cesar PF, Miranda WG Jr & Braga RR (2001) Influence of shade and storage time on the flexural strength, flexural modulus, and hardness of composites used for indirect restorations *Journal of Prosthetic Dentistry* **86(3)** 289-296.
14. Bouschlicher MR, Rueggeberg FA & Wilson BM (2004) Correlation of bottom-to-top surface microhardness and conversion ratios for a variety of resin composite compositions *Operative Dentistry* **29(6)** 698-704.
15. Ferracane JL (1985) Correlation between hardness and degree of conversion during the setting reaction of unfilled dental restorative resins *Dental Materials* **1(1)** 11-14.
16. Ruggeberg FA & Craig RG (1988) Correlation of parameters used to estimate monomer conversion in a light-cured composite *Journal of Dental Research* **67(6)** 932-937.
17. Hofmann N, Hugo B & Klaiber (2002) Effect of irradiation type (LED or QTH) on photo-activated composite shrinkage strain kinetics, temperature rise, and hardness *European Journal of Oral Sciences* **110(6)** 471-479.
18. Uhl A, Mills RW & Jandt KD (2003) Photoinitiator dependent composite depth of cure and Knoop hardness with halogen and LED light curing units *Biomaterials* **24(10)** 1787-1795.
19. deMoraeus PR, Goncalves Lde S, Lancelloti AC, Consani S, Correr-Sobrinho L & Sinhoreti MA (2009) Nanohybrid resin composite: Nano filler loaded materials or traditional microhybrid resins? *Operative Dentistry* **34(5)** 551-557.

20. Korkmaz Y, Ozel E, Attar N & Aksoy G (2008) The influence of one-step polishing systems on the surface roughness and microhardness of nanocomposites *Operative Dentistry* **33(1)** 44-50.

21. Calheiros FC, Kawano Y, Stansbury JW & Bragga RR (2006) Influence of radiant exposure on contraction stress, degree of conversion and mechanical properties of resin composites *Dental Materials* **22(9)** 799-803.

22. Andrzejewska E (2004) Kinetics of network formation during photopolymerization *Transactions of Academy of Dental Materials* **18(10)** 69-80.

23. Hasler C, Zimerli B & Lussi A (2006) Curing capability of Halogen and LED light curing units in deep Class II cavities in extracted human molars *Operative Dentistry* **31(3)** 354-363.

24. Arikawa H, Fujii K, Kanie T & Inoue K (1998) Light transmittance characteristics of light cured composite resins *Dental Materials* **14(6)** 405-411.