

Comparative study of surface microhardness of methacrylate-based composite resins polymerized with light-emitting diodes and halogen

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ABSTRACT

Objective: The aim of this study was to evaluate the effect of polymerization with quartz-tungsten-halogen (QTH) and light-emitting diodes (LED) on the surface microhardness of eight commercially available light-polymerized, methacrylate-based composite resins, with different filler particle composition (microfill, minifill, nanohybrids, and microhybrids) immediately after polymerization, after 24 hours, and after three months of storage. **Materials and Methods:** Eighty disk-shaped specimens were prepared using a split Teflon mold (6 × 2 mm) and were irradiated with either the QTH (Elipar 2500; 600 mW/cm²) for 20 seconds or an LED (Bluephase G2; 1,200 mW/cm²) for 40 seconds. The microhardness values were recorded using a Vickers hardness tester at a 300 g load for 15 seconds, immediately after polymerization, after 24 hours, and after three months of dark aging in distilled water at 37°C. Statistical analysis was performed using a two-way analysis of variance (ANOVA) and the Tukey's test. **Results:** The baseline values demonstrated a significant effect of the composite and the interaction composite-LCU on the microhardness ($P < 0.05$). At 24 hours, only the composite variable showed a significant effect on the hardness values ($P < 0.05$). After three months, the composite, LCU, and the interaction composite-LCU all demonstrated a significant effect on the microhardness ($P < 0.05$). **Conclusions:** The effectiveness of polymerization, measured in terms of surface hardness, was shown to be dependent not only on the type of light curing unit, but also on the type of composite. Moreover, the choice of composite was shown to affect the performance of the light curing unit.

Key words: Composite resin, halogen, light-emitting diodes, microhardness, polymerization

INTRODUCTION

A number of aspects play a role in the success of composite resin restorations. Composites' mechanical and physical properties are dependent on the degree of polymerization.^[1] The extent of polymerization is in turn dependent on the aspects relative to the material's composition and the amount of energy delivered to the material. Aspects such as composite type, size, amount of inorganic filler loading, resin matrix composition, and the type and concentration of the photoinitiator,^[2] as well as the wavelength of the emitted light, bulb intensity, exposure time, and distance and angulation of the light tip^[3] are all known to affect the composites' degree of polymerization.

Light-activated composites polymerize by free radical polymerization, whereby methacrylate carbon-carbon double bonds become available for cross-linking monomers into polymeric chains.^[4] Most composite resin systems use camphorquinone (CQ), which has an absorption peak of 468 nm, as their photoinitiator. When exposed to blue light of wavelength in the range of 400 to 500 nm, CQ reacts with an amine activator to form free radicals, initiating the polymerization reaction.^[5] Approximately 75% of the polymerization reaction takes place during the first 10 minutes,^[6,7] after which composites undergo a post-irradiation polymerization reaction that lasts up to 24 hours.^[8] This dark cure has been shown to be quite extensive, with as much as 19-26% of the final monomer conversion

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taking place during this period.^[9] However, the conversion of C = C is not complete; a heterogeneous structure with densely cross-linked and poorly cross-linked areas is generated.^[10]

Halogen and light-emitting diodes (LEDs) represent the most commonly used light curing units (LCUs) for the polymerization of light-activated composites. Halogen's broad emission spectrum allows the polymerization of a wide range of composite materials. However, filters that reduce heat energy transfer are required to decrease the output of undesired wavelengths and deliver light in the 410-500 nm region of the visible spectrum.^[5] Drawbacks associated with the degradation of these filters have been reported to result in inadequately polymerized restorations.^[11] LEDs convert electricity into light more efficiently,^[12] thereby, eliminating the need for additional filters to generate blue light. Their narrow wavelength spectrum matches, more closely, the absorption peak of CQ.^[13] Moreover, they can operate for thousands of hours with a constant light output,^[14] and the higher irradiances allow reduced polymerization times.^[15]

Issues derived from insufficient polymerization and residual unreacted monomers have been reported to compromise the polymer mechanical properties.^[16,17] Poor surface characteristics resulting from insufficient polymerization are equally important, as they may result in premature degradation, wear, and staining.^[18,19] As improved formulations of composite resin materials continue to be developed and to provide a wide range of clinical applications, it becomes essential that studies continue to be undertaken to evaluate their mechanical and physical properties when polymerized with different LCUs. Because of the good correlation observed between hardness measurements and the degree of monomer conversion, hardness tests are commonly used as an indirect assessment of the extent of polymerization of composites.^[20-22]

Therefore, the aim of this study was to evaluate the surface microhardness of eight commercially available light-polymerized, methacrylate-based composite resins with different filler particle composition (microfill, minifill, nanohybrids, and microhybrids) polymerized with quartz-tungsten-halogen (QTH) and light-emitting diodes (LEDs) immediately after polymerization, after 24 hours, and after three months of storage. The following null hypotheses were tested: (1) There would be no influence of the polymerization unit, when delivering equivalent energy densities, on the

surface microhardness of eight methacrylate-based composite resin materials. (2) There would be no influence of the type of composite on the surface microhardness following polymerization with an LED or QTH.

MATERIALS AND METHODS

Microhardness of eight commercially available light-polymerized, methacrylate-based composite resins was evaluated in this study. Tetric EvoCeram, Premise, Artiste, Beautifil II (nanohybrids), Filtek Supreme Plus, and Vit-I-escence (microhybrids), Heliomolar (microfill), and Estelite Sigma Quick (minifill), in shade A3 enamel, were polymerized with either LED or halogen LCUs. The composites and LCUs were selected to represent a range of commonly used products. Table 1 summarizes the composition and energy requirements of the composites evaluated in this study as per the manufacturer's description. Five disks were prepared per study group ($n = 5$) for a total of 80 specimens, as determined by the preliminary power analysis.

The specimens were prepared by condensing the composite into a white polytetrafluoroethylene (PTFE) split mold (diameter: 6 mm; height: 2 mm) against a microscope glass slab, with a mylar strip between the glass slab and the PTFE mold, to avoid oxygen inhibition and with care to avoid air entrapment. A second mylar strip and glass slab were stabilized in contact with the uncured composite and pressed to the thickness of the mold. Glass slabs were used to provide flat specimens with a uniform surface that would be less likely to introduce variations in the microhardness measurements. The split molds were held together by an adjustable metal frame, which also served as a spacer providing a standardized distance of 1 mm between the light tip and the surface of the composite.

Two LCUs were used for photoactivation of the composite specimens: A halogen bulb unit (Elipar 2500, 3M ESPE, St Paul, MN, USA; 600 mW/cm²) and an LED unit (Bluephase G2, Ivoclar-Vivadent, Amherst, NY, USA; 1,200 mW/cm²) with light probe diameters of 8 mm and 10 mm, respectively. The light curing tip was placed at 90° with respect to the surface. The irradiances of the LCUs were measured using a hand held LED radiometer (Demetron, Kerr, Orange, CA, USA). The total energy requirement for optimal polymerization of the composites, referred to as radiant exposure, was calculated as the product of the irradiance and the irradiation time recommended by

Table 1: Resin composite brands, categories, and composition as per manufacturer's description

Product (Manufacturer)	Code	Lot	Category	Matrix	Photo- initiator	Energy required* (J/cm ²)	Particle size (µm) (Mean)	Filler type	Filler content	
									%wt	%vol
Estelite Sigma Quick (Tokuyama, Tokyo, Japan)	EQ	E674	Minifill	Bis-GMA, TEGDMA	CQ/ RAP	4.5-6	0.1-0.3 (0.2)	Zirconia-silica, composite filler	82	71
Heliomolar (Ivoclar-Vivadent, Amherst, NY)	HM	M00783	Microfill	Bis-GMA, UDMA, Decandiol dimethacrylate	CQ/ amine	20	0.04-0.2	Silicon dioxide, ytterbium trifluoride, pre-polymers	66,7	46
Tetric EvoCeram (Ivoclar-Vivadent, Amherst, NY)	TEC	N58533	Nanohybrid	Dimethacrylates	CQ/ amine	10	0.04- 3.0 (0.55)	Barium glass, ytterbium trifluoride, mixed oxide, pre-polymers	75-76	53-55
Premise (Kerr, Orange, CA)	PR	3204934	Nanohybrid	Bis-EMA, TEGDMA	CQ/ amine	10	PPF, 30-50 Silica, 0.02 Barium, 0.4	Pre-polymerized filler, barium glass, silica filler	84	70
Artiste (Pentron, Wallingford, CT)	AR	167373	Nanohybrid	PCBisGMA/ BisGMA/ UDMA/HDDMA	Not reported	8.0-12	0.02-0.7	Barium boro-alumino silicate glass, nano-particulated silica, zirconium silicate	75	66
Beautiful II (Shofu, Kyoto, Japan)	BII	051026-51	Giomer Nanohybrid	Bis-GMA, TEGDMA	CQ/ amine	10	0.01-4.0 (0.8)	Glass filler, S-PRG filler (fluoroboroaluminosilicate glass)	83,3	68,6
Filtek Supreme Plus (3M-ESPE, St. Paul, MN)	FSP	8EA	Micro-hybrid	Bis-GMA, Bis-EMA, UDMA, TEGDMA, PEGDMA	CQ/ amine	24	Clusters, 0.6-1.4; Silica, 0.02	Silica filler, zirconia filler, aggregated zirconia/silica	78,5	59,5
Vit-L-Escence (Ultradent, South Jordan, UT)	VL	B4869	Micro-hybrid	Bis-GMA	CQ/ amine	9,2	0,7	Barium alumina silicate	75	58

(* The energy requirement was calculated based on the information provided from the manufacturer regarding time and light curing unit recommended for polymerization, Bis-GMA: Bisphenol A glycidyl dimethacrylate, Bis-EMA: Ethoxylated bisphenol A dimethacrylate, CQ: Camphorquinone, HDDMA: Hexanediol dimethacrylate, PCBis-GMA: Polycarbonate modified-BisGMA, PEGDMA: Poly (ethylene glycol) dimethacrylate, PPF: Pre-polymerized filler, RAP: Radical amplified photopolymerization, TEGDMA: Triethylene glycol dimethacrylate, UDMA: Urethane dimethacrylate

the manufacturer. The radiant exposure values ranged from 4.5 to 24 J/cm² [Table 1]. If the manufacturer only provided recommendations regarding the irradiation time, the irradiance of the LCU recommended by the manufacturer was used to calculate the radiant exposure. For standardization of the amount of energy delivered to the composites, all specimens received 24 J/cm². To deliver a radiant exposure of 24 J/cm², the irradiation time was set to 20 seconds for the LED (1,200 mW/cm² × 20 seconds) and 40 seconds for the halogen (600 mW/cm² × 40 seconds). Immediately after polymerization, the baseline surface microhardness values were recorded using a Vickers hardness tester (MicroMet 5104, Buehler, Lake Bluff, IL, USA) with a diamond pyramid micro-indenter. The test was conducted at room temperature (23°C) under a load of 300 g with a dwell time of 15 seconds. Five indentations, 1 mm apart, were made on the irradiated surface of the specimen and averaged to yield a single microhardness number. The x- and y-axes were measured by observation through the

optical microscope at a magnification of 50x. The specimens were then incubated in distilled water in a dark environment at 37°C. Subsequent microhardness measurements were recorded after 24 hours and three months.

Separate two-way analysis of variance (ANOVA) tests were used to evaluate the effect of the main variables – composite and LCU – and their interactions on the microhardness at each of the testing periods. A post-hoc Tukey's test was used for pairwise multiple comparisons of group means. In addition, for each composite-LCU combination, a one-way ANOVA and post-hoc Student-Newman-Keuls test were used to investigate the differences among the baseline hardness values, and values after 24 hours and three months. A significance level of $P < 0.05$ was used for all the tests. All statistical analyses were performed using the Statistical Package for Social Sciences (SPSS) version 16.0 (SPSS Inc, Chicago, IL, USA).

RESULTS

Evaluation of the hardness values immediately after polymerization by the two-way ANOVA revealed a significant effect of the composite ($P < 0.001$) and the interaction between composite and LCU ($P = 0.032$), but no effect of the LCU on the microhardness was observed. Post-hoc multiple comparisons with the Tukey's test revealed significant differences among the composites for both LCUs [Table 2]. For most brands, no significant differences in hardness values were demonstrated when the composites were polymerized with either the halogen or the LED, except for Tetric EvoCeram ($P = 0.015$) and Premise ($P = 0.019$), which showed significantly higher hardness when polymerized with the halogen.

After 24 hours, a significant effect on microhardness was demonstrated for the composite ($P = 0.002$), but not for the LCU or the interaction between the composite and LCU. No significant differences among composites were observed when the specimens were polymerized with LED [Table 3]. Conversely, when composites were polymerized with the halogen, significant differences among composites were evidenced [Table 3]. Overall, no significant differences

in hardness values were present when composites were polymerized with either the halogen or LED, except for Filtek Supreme Plus, which demonstrated significantly higher hardness when polymerized with the halogen ($P = 0.015$).

Evaluation of the hardness values after three months revealed a significant effect of the composite ($P < 0.001$), LCU ($P < 0.001$), and the interaction between the composite and LCU ($P < 0.001$) on the microhardness. Significant differences among composites were evidenced for both LCUs [Table 4]. For all composites, polymerization with the halogen yielded significantly higher hardness values ($P < 0.001$).

One-way ANOVA for each composite-LCU combination revealed no significant differences in microhardness values among the different testing periods, with only a few exceptions [Figure 1]. After LED-polymerization, significantly lower hardness values after three months were seen for Artiste, relative to its 24-hour values ($P < 0.05$), and for Estelite Sigma Quick relative to its baseline values ($P < 0.05$). After polymerization with the halogen, Heliomolar demonstrated significantly higher hardness values after three months relative to its baseline ($P = 0.005$)

Table 2: Mean surface microhardness immediately after polymerization with LED and QTH

	Heliomolar	Tetric evo ceram	Vit-I-escence	Filtek supreme plus	Premise	Artiste	Beautifil II	Estelite sigma quick
LED baseline	34.1±9.7 ^{b,1}	69.5±11.2 ^{a,b,1}	88.3±18.3 ^{a,1}	96.8±33.6 ^{a,1}	80.2±20.2 ^{a,1}	85.3±30.6 ^{a,1}	89.1±26.7 ^{a,1}	103.7±27.4 ^{a,1}
QTH baseline	36.8±14.4 ^{c,1}	103.1±17.2 ^{a,2}	97.4±16.8 ^{a,b,1}	80.6±12.7 ^{a,b,1}	112.5±14.1 ^{a,2}	60.3±15.5 ^{b,c,1}	99.3±33.0 ^{a,b,1}	104.5±28.6 ^{a,1}

Same superscript letter indicates no significant difference between composites for each LCU (rows), Same superscript number indicates no significant difference between LCUs for each composite (columns), LED: Light-emitting diodes, QTH: Quartz-tungsten-halogen

Table 3: Mean surface microhardness 24 hours after polymerization with LED and QTH

	Heliomolar	Tetric evo ceram	Vit-I-escence	Filtek supreme plus	Premise	Artiste	Beautifil II	Estelite sigma quick
LED 24 h	54.9±27.1 ^{a,[1]}	77.8±35.0 ^{a,1}	94.8±31.5 ^{a,1}	91.9±36.1 ^{a,1}	81.4±62.9 ^{a,1}	110.9±48.0 ^{a,1}	95.1±64.1 ^{a,1}	76.8±22.5 ^{a,1}
QTH 24 h	40.5±12.4 ^{c,1}	119.7±21.3 ^{a,b,1}	92.3±23.4 ^{a,b,c,1}	145.6±35.5 ^{a,2}	103.7±28.6 ^{a,b,c,1}	76.6±22.9 ^{b,c,1}	109.1±32.5 ^{a,b,1}	77.1±33.3 ^{b,c,1}

Same superscript letter indicates no significant difference between composites for each LCU (rows), Same superscript number indicates no significant difference between LCUs for each composite (columns), LED: Light-emitting diodes, QTH: Quartz-tungsten-halogen

Table 4: Mean surface microhardness three months after polymerization with LED and QTH

	Heliomolar	Tetric evo ceram	Vit-I-escence	Filtek supreme plus	Premise	Artiste	Beautifil II	Estelite sigma quick
LED 3 months	42.0±10.6 ^{d,1}	44.5±2.8 ^{d,1}	66.5±6.0 ^{a,1}	71.0±5.0 ^{a,1}	54.8±2.2 ^{b,c,1}	48.5±2.3 ^{c,d,1}	65.7±5.6 ^{a,1}	55.9±2.6 ^{b,1}
QTH 3 months	66.9±5.8 ^{f,2}	90.1±4.0 ^{c,d,2}	101.0±4.3 ^{b,2}	110.4±4.3 ^{a,2}	97.0±4.2 ^{b,c,2}	88.2±4.6 ^{d,2}	75.3±6.6 ^{e,2}	76.0±5.8 ^{e,2}

Same superscript letter indicates no significant difference between composites for each LCU (rows), Same superscript number indicates no significant difference between LCUs for each composite (columns), LED: Light-emitting diodes, QTH: Quartz-tungsten-halogen

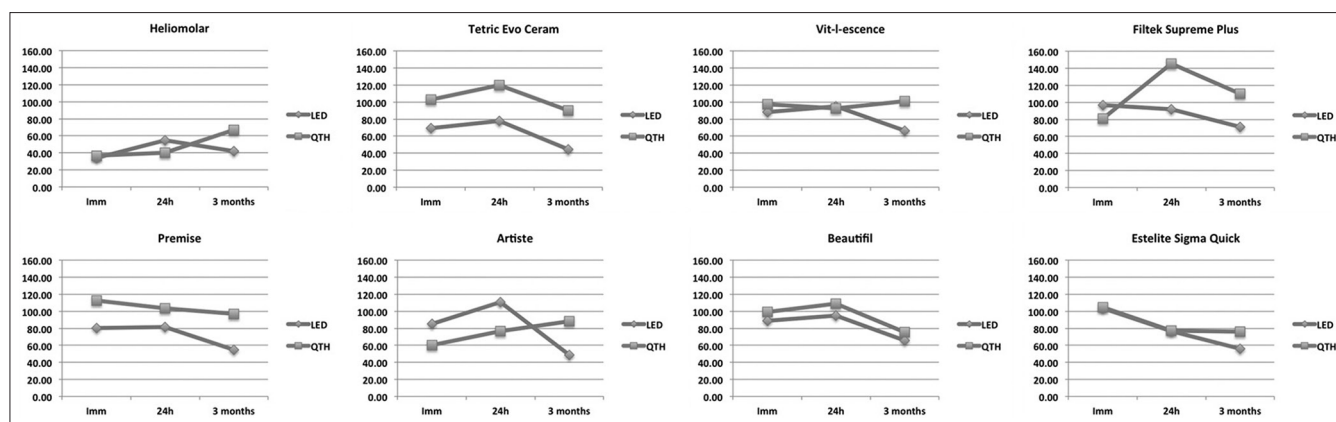


Figure 1: Mean surface microhardness of composites polymerized with LED and halogen immediately after polymerization, at 24 hours and three months

and 24-hour values ($P = 0.004$), Tetric EvoCeram yielded significantly lower hardness values after three months compared to its 24-hour values ($P = 0.018$), and Filtek Supreme Plus showed significantly higher hardness values at 24 hours relative to its baseline values ($P < 0.05$).

DISCUSSION

The present study evaluated the surface microhardness of eight methacrylate-based composites with different filler particle composition: Tetric EvoCeram, Premise, Artiste, Beautifil II (nanohybrids), Filtek Supreme Plus and Vit-I-escence (microhybrids), Heliomolar (microfill), and Estelite Sigma Quick (minifill) polymerized, with either halogen or LED, after different storage periods. As the surface characteristics largely determine the future wear and permeability behavior of the polymer, it was the primary focus of our study to evaluate the surface hardness characteristics of the various composites when polymerized with the different LCUs. The composites and LCUs included in our study were selected to represent a wide range of commonly used products. We also investigated changes in surface hardness characteristics over time for the different composite-LCU combinations.

The first null hypothesis was only partially accepted. No significant effect of the LCU was demonstrated when hardness was evaluated at baseline or at 24 hours. Evaluation of the three-month values, however, revealed a significant effect of the LCU on microhardness, which resulted in partial rejection of the first null hypothesis. The second null hypothesis was rejected. A significant effect of the composite on microhardness was demonstrated at all testing periods,

irrespective of the LCU. Significant interactions between the composite and LCU were also demonstrated both at baseline and after three months, indicating that the surface hardness of the composites was dependent on the type of LCU used for polymerization. This was coincident with previous studies, which have demonstrated that the choice of composite affects the performance of LCUs.^[2,13,23,24] However, a number of aspects play a role in the polymerization kinetics of composites, and thus, no definitive statements can be made as to the ability of the different composite-LCU combinations to polymerize.

Effect of the light curing unit

Evaluation of the hardness values immediately after polymerization and at 24 hours showed no significant differences between the specimens polymerized with LED and halogen, with only a few exceptions: Tetric EvoCeram and Premise at baseline and Filtek Supreme Plus at 24 hours demonstrated significantly higher hardness values when polymerized with halogen. When the microhardness values were evaluated after three months, significantly higher values were seen for specimens polymerized with halogen, for all composites. The observed differences in hardness values at baseline and 24 hours revealed variations in the extent of polymerization, which might be the result of aspects relative to material composition and the amount of energy delivered during polymerization. Conversely, evaluation of the hardness values after three months incorporated the additional effect of aging conditions, such as water sorption and polymer swelling, which were expected to affect the specimens to various degrees depending on the extent of polymer network cross-linking achieved initially after photoactivation. Less unreacted monomer,^[25] with the consequent greater hardness has previously been

reported for composites polymerized with halogen compared to LED. However, the evidence in the subject remains inconclusive, with studies showing no difference in hardness values when polymerization was done with LED and conventional or high-intensity QTH,^[26] and studies showing greater extent of cure^[27,28] and surface hardness^[29] for LED-polymerized composites.

A number of aspects are known to affect the extent of polymerization of composite materials. In theory, delivering the same radiant exposure to the surface should result in an equivalent degree of polymerization, irrespective of the type of LCU. Manufacturers normally do not provide information regarding the radiant exposure or the amount of energy required to ensure optimal polymerization of their composites. This information is of great clinical relevance, and it should be provided in their product description. Instead, only recommendations regarding polymerization time are provided, and general terms such as 'standard light' or 'high-intensity light' are used to describe the type and mode of LCU recommended, resulting in a vague estimation of the energy requirements. An approximate total energy value required for optimal polymerization of a composite can be calculated as the product of the irradiance and the irradiation time recommended by the manufacturer. However, since the exact energy requirements for maximum curing efficiency remain unclear,^[30] it is common to over-irradiate restorations to avoid issues derived from under-polymerization, such as secondary caries, marginal breakdown, and wear. It has been reported that depending on the brand and shade of the composite, as little as 6 J/cm² or as much as 36 J/cm² is required to adequately cure a 2-mm increment of resin.^[31] In our study, the total energy requirement for polymerization of the different composites ranged from 4.5 to 24 J/cm². For standardization of the amount of energy delivered to the composites, the highest recommended value, 24 J/cm², was used for the polymerization of all composites, as no further conversion was expected to occur as a result of over-polymerization.^[32] A correlation has been shown between the amount of energy delivered to a composite and the resulting degree of conversion and physical properties;^[33] however, this relationship is not linear and no further increase in monomer conversion is known to occur above a certain radiant exposure value.^[32]

Other aspects may also be responsible for variations in the extent of polymerization, and therefore, in the

hardness of composites. First, the information on the output irradiance generated by dental radiometers is not very accurate.^[34] Since the irradiance distribution over the light guide tip is not homogeneous, readings from dental radiometers, aside from being inaccurate, only provide an average of the irradiance delivered over the whole diameter of the light guide, which does not represent the irradiance actually delivered to the composite molds.^[24] An accurate measurement of the irradiance and spectral irradiance can be obtained with resin calibrators such as MARC-RC or MARC-PS. Moreover, despite a known radiant exposure value, the amount of energy delivered by the LCU is not equivalent to the energy actually received by the composite surface. Since the light output is rarely a uniform beam and the center of the beam often delivers considerably greater irradiance,^[35,36] the center of the composite specimen is often better polymerized than its peripheral area.^[36] In our study, light probe diameters of 8 mm and 10 mm for the halogen and LED, respectively, were used for the polymerization of specimens that were 6 mm in diameter. By using light probes with diameters greater than those of the composite specimens, the use of peripheral lower-irradiance energy was minimized in the polymerization of the samples. Furthermore, five hardness measurements, one central and four peripheral, were recorded to provide an average of the surface hardness readings. In addition, as increased distances from the light-curing probe to the composite surface are known to result in loss of intensity,^[37] and because a distance of 0 mm to the composite surface is of very limited relevance since this rarely reflects the clinical situation, this distance was standardized to 1 mm by using a metal mold, based on recommendations from previous studies.^[37,38] Additional factors such as degradation of the halogen built-in filters, which is known to occur undetected over time, may have also compromised the amount of energy delivered to the samples,^[11] perhaps yielding variations in the hardness results.

Effect of the composite

Coincident with results from previous studies,^[39] microhardness values were also shown to be dependent on the type of composite. The composites included in this study were selected to represent a wide range of commercially available materials with different filler particle composition. A correlation between hardness values and filler loading was demonstrated for materials in opposite ends of the spectrum. Heliomolar, with the lowest filler content, resulted in the lowest hardness values,

while highly filled materials, such as Filtek Supreme Plus, Estelite, and Premise, yielded the highest hardness values. Heliomolar is made from fumed silica with an average particle size of 40 nm, which results in a relative low filler loading. Although pre-polymerized filler particles are incorporated to increase the filler content of traditional microfills, they still exhibit substantially lower filler loading than microhybrids. Conversely, the wide range of particle sizes in microhybrids and nanohybrids allows for greater filler content and a consequent higher strength. Filtek Supreme Plus contains a combination of 20 to 75 nm nanofillers and loosely bound agglomerates of nanosized particles that behave as a single unit, enabling high filler loading, and thus, high strength.

Studies have previously demonstrated lower hardness values for microfilled composites relative to microhybrids.^[40-42] This may be explained not only by the greater organic resin matrix content, which is known to produce a less cross-linked polymer network, but also by the greater light scattering derived from the small filler size of microfilled composites, which compromises the effectiveness of polymerization. Filler particles are known to scatter light, and both filler size and content influence light dispersion.^[43] Smaller filler particles, such as microfills (0.01-0.1 μm) and minifills (0.1-1.0 μm), scatter more light than microhybrids, which contain a combination of different particle sizes.^[43] As the light beam becomes scattered and reflected within the composite material, it loses intensity, with the consequent adverse effect on the degree of polymerization.^[43]

The nature of the resin matrix has also been reported to affect the hardness and overall mechanical properties of composites. TEGDMA is known to create a much more dense network than Bis-GMA.^[44] Newer formulations of composites incorporate an increased TEGDMA content, a more reactive diluent monomer (α -methylene- γ -butyrolactone), carboxylic anhydrides, aldehydes, and diketones, all of which allow increased polymer matrix cross-linking, with the consequent improved mechanical and physical properties.^[43] However, manufacturers normally do not disclose proprietary information regarding the specific composition of their materials, and thus, correlations based merely on material composition cannot be established.

The type and concentration of the photoinitiator is also known to influence the curing efficiency of the

composite.^[45] All composites evaluated in our study use CQ as their photoinitiator. Nevertheless, the concentration of CQ and the presence of any other unreported photoinitiators in the mixture are both unknown, and thus, no associations may be drawn with the observed results. A study demonstrated that two of the composites evaluated in our study, Tetric EvoCeram and Vit-l-escence, contain TPO in their composition.^[46] The manufacturers of these products, however, do not report this information in their product description. Photoinitiators such as TPO have a lower absorption peak of around 380 nm,^[45] and hence, a less cross-linked polymer may be the result of polymerization with a narrow bandwidth LED unit. In our study, a poly-wave LED unit with a broadband spectrum between 380 and 515 nm was used. The wider emission spectrum, comparable to that of halogen lights, allows curing of composites containing all photoinitiator systems; thus, the differences in hardness values observed for Tetric EvoCeram polymerized with either halogen or LED cannot be attributed to these additional unreported co-initiators.

Effect of the storage time

Hardness tests most commonly report results obtained immediately after polymerization, at 24 hours, and a few days following initial photoactivation. Typically, an increase in hardness values is observed in the first few hours/days following initial photoactivation, due to a continued polymerization reaction. Results from long-term storage, conversely, provide information regarding the effect of different aging conditions, such as water sorption, thermal variations, and wear, in the stability of the polymer network. Although the main purpose of this study was not to assess changes in hardness values over time, comparisons among baseline, 24 hours, and three-month hardness values were also conducted for each composite-LCU combination. Overall, most composites demonstrated an increase in hardness values after 24 hours, which was followed by a decrease in hardness after three months of storage. Only a few exceptions were observed, as shown in Figure 1. Despite the observed trends, the differences remained not significant for most composite-LCU combinations. Our results are in agreement with previous studies, which have shown that there is typically an increase in hardness values during the first 24 hours following polymerization.^[47]

After three months, a decrease in hardness values was seen for most composite-LCU combinations, which was more noticeable for some materials. The same

aging conditions affected the stability of the polymer network of the various composite-LCU combinations differently, perhaps based on the extent of their initial cross-linking. These results also remained not significant and only a few exceptions of increased hardness values after three months were observed. Heliomolar polymerized with halogen was the only combination that showed a significant increase in hardness values after three months relative to both baseline and 24 hours. Future studies should explore the presence of correlations between initial hardness values and the rate at which composite materials degrade over time.

CONCLUSIONS

Within the limitations of this *in vitro* study, the following can be concluded:

- When delivering equivalent energy densities, polymerization with the halogen or LED did not have a significant effect in microhardness values either at baseline or after 24 hours. After three months, a significant effect of the LCU was evident with significantly higher hardness values when all composites were polymerized with the halogen.
- A significant effect of the type of composite on the microhardness values was shown at all testing periods, irrespective of the LCU.
- Significant interactions between the composite and LCU were also evident at baseline and after three months, indicating that the surface hardness of the composites was dependent on the type of LCU used for polymerization.

REFERENCES

1. Tseng WY, Huang CH, Chen RS, Lee MS, Chen YJ, Rueggeberg FA, *et al.* Monomer conversion and cytotoxicity of dental composites irradiated with different modes of photoactivated curing. *J Biomed Mater Res B Appl Biomater* 2007;83:85-90.
2. Leonard DL, Charlton DG, Roberts HW, Cohen ME. Polymerization efficiency of LED curing lights. *J Esthet Restor Dent* 2002;14:286-95.
3. Aravamudhan K, Rakowski D, Fan PL. Variation of depth of cure and intensity with distance using LED curing lights. *Dent Mater* 2006;22:988-94.
4. Peutzfeldt A. Resin composites in dentistry: The monomer systems. *Eur J Oral Sci* 1997;105:97-116.
5. Rueggeberg F. Contemporary issues in photocuring. *Compend Contin Educ Dent Suppl* 1999;54:15; quiz S73.
6. Chung KH, Greener EH. Correlation between degree of conversion, filler concentration and mechanical properties of posterior composite resins. *J Oral Rehabil* 1990;17:487-94.
7. Ferracane JL, Greener EH. The effect of resin formulation on the degree of conversion and mechanical properties of dental restorative resins. *J Biomed Mater Res* 1986;20:121-31.
8. Eliades GC, Vougiouklakis GJ, Caputo AA. Degree of double bond conversion in light-cured composites. *Dent Mater* 1987;3:19-25.
9. Halvorson RH, Erickson RL, Davidson CL. Energy dependent polymerization of resin-based composite. *Dent Mater* 2002;18:463-9.
10. Sideridou I, Tserki V, Papanastasiou G. Effect of chemical structure on degree of conversion in light-cured dimethacrylate-based dental resins. *Biomaterials* 2002;23:1819-29.
11. Mills RW, Uhl A, Blackwell GB, Jandt KD. High power light emitting diode (LED) arrays versus halogen light polymerization of oral biomaterials: Barcol hardness, compressive strength and radiometric properties. *Biomaterials* 2002;23:2955-63.
12. Price RB, Felix CA, Andreou P. Knoop hardness of ten resin composites irradiated with high-power LED and quartz-tungsten-halogen lights. *Biomaterials* 2005;26:2631-41.
13. Uhl A, Sigusch BW, Jandt KD. Second generation LEDs for the polymerization of oral biomaterials. *Dent Mater* 2004;20:80-7.
14. Ruttermann S, Tomruk S, Raab WH, Janda R. Effect of energy density on the physical properties of resin-based restorative materials when polymerized with quartz-tungsten halogen or LED-light. *Eur J Dent* 2010;4:183-91.
15. Fleming GJ, Awan M, Cooper PR, Sloan AJ. The potential of a resin-composite to be cured to a 4mm depth. *Dent Mater* 2008;24:522-9.
16. Ferracane JL. Correlation between hardness and degree of conversion during the setting reaction of unfilled dental restorative resins. *Dent Mater* 1985;1:11-4.
17. Mills RW, Jandt KD, Ashworth SH. Dental composite depth of cure with halogen and blue light emitting diode technology. *Br Dent J* 1999;186:388-91.
18. Dietschi D, Campanile G, Holz J, Meyer JM. Comparison of the color stability of ten new-generation composites: An *in vitro* study. *Dent Mater* 1994;10:353-62.
19. Doray PG, Wang X, Powers JM, Burgess JO. Accelerated aging affects color stability of provisional restorative materials. *J Prosthodont* 1997;6:183-8.
20. Santos GB, Medeiros IS, Fellows CE, Muench A, Braga RR. Composite depth of cure obtained with QTH and LED units assessed by microhardness and micro-Raman spectroscopy. *Oper Dent* 2007;32:79-83.
21. Rode KM, Kawano Y, Turbino ML. Evaluation of curing light distance on resin composite microhardness and polymerization. *Oper Dent* 2007;32:571-8.
22. da Silva EM, Poskus LT, Guimaraes JG. Influence of light-polymerization modes on the degree of conversion and mechanical properties of resin composites: A comparative analysis between a hybrid and a nanofilled composite. *Oper Dent* 2008;33:287-93.
23. Uhl A, Michaelis C, Mills RW, Jandt KD. The influence of storage and indenter load on the Knoop hardness of dental composites polymerized with LED and halogen technologies. *Dent Mater* 2004;20:21-8.
24. Uhl A, Mills RW, Jandt KD. Photoinitiator dependent composite depth of cure and Knoop hardness with halogen and LED light curing units. *Biomaterials* 2003;24:1787-95.
25. Filipov IA, Vladimirov SB. Residual monomer in a composite resin after light-curing with different sources, light intensities and spectra of radiation. *Braz Dent J* 2006;17:34-8.
26. Yazici AR, Kugel G, Gul G. The Knoop hardness of a composite resin polymerized with different curing lights and different modes. *J Contemp Dent Pract* 2007;8:52-9.
27. Hasler C, Zimmerli B, Lussi A. Curing capability of halogen and LED light curing units in deep class II cavities in extracted human molars. *Oper Dent* 2006;31:354-63.
28. Ye Q, Wang Y, Williams K, Spencer P. Characterization of photopolymerization of dentin adhesives as a function of light source and irradiance. *J Biomed Mater Res B Appl Biomater* 2007;80:440-6.
29. Campregher UB, Samuel SM, Fortes CB, Medina AD, Collares FM, Ogliari FA. Effectiveness of second-generation light-emitting diode (LED) light curing units. *J Contemp Dent Pract* 2007;8:35-42.
30. Rueggeberg FA. State-of-the-art: Dental photocuring: A review. *Dent Mater* 2011;27:39-52.
31. Calheiros FC, Kawano Y, Stansbury JW, Braga RR. Influence of radiant exposure on contraction stress, degree of conversion and mechanical properties of resin composites. *Dent Mater* 2006;22:799-803.
32. Calheiros FC, Braga RR, Kawano Y, Ballester RY. Relationship between contraction stress and degree of conversion in restorative composites. *Dent Mater* 2004;20:939-46.
33. Halvorson RH, Erickson RL, Davidson CL. Energy dependent polymerization of resin-based composite. *Dent Mater* 2002;18:463-9.
34. Roberts HW, Vandewalle KS, Berzins DW, Charlton DG. Accuracy of

- LED and halogen radiometers using different light sources. *J Esthet Restor Dent* 2006;18:214-22.
35. Vandewalle KS, Roberts HW, Andrus JL, Dunn WJ. Effect of light dispersion of LED curing lights on resin composite polymerization. *J Esthet Restor Dent* 2005;17:244-54.
 36. Vandewalle KS, Roberts HW, Rueggeberg FA. Power distribution across the face of different light guides and its effect on composite surface microhardness. *J Esthet Restor Dent* 2008;20:108-17.
 37. Pires JA, Cvitko E, Denehy GE, Swift EJ Jr. Effects of curing tip distance on light intensity and composite resin microhardness. *Quintessence Int* 1993;24:517-21.
 38. Sobrinho LC, de Lima AA, Consani S, Sinhoreti MA, Knowles JC. Influence of curing tip distance on composite Knoop hardness values. *Braz Dent J* 2000;11:11-7.
 39. Giorgi MC, Aguiar FH, Soares LE, Martin AA, Liporoni PC, Paulillo LA. Does an additional UV LED improve the degree of conversion and Knoop Hardness of light-shade composite resins? *Eur J Dent* 2012;6:396-401.
 40. Dunn WJ, Bush AC. A comparison of polymerization by light-emitting diode and halogen-based light-curing units. *J Am Dent Assoc* 2002;133:335-41.
 41. Giorgi MC, Sartini Paulillo LA. Knoop hardness of composites cured with halogen and led light-curing units in class I restorations. *Braz J Oral Sci* 2009;8:30-3.
 42. Leonard DL, Charlton DG, Roberts HR, Hilton TJ, Zionis A. Determination of the minimum irradiance required for adequate polymerization of hybrid and microfill composite. *Oper Dent* 2001;26:176-80.
 43. Malhotra N, Mala K. Light-curing considerations for resin-based composite materials: A review. Part II. *Compend Contin Educ Dent* 2010;31:584-8, 590-1; quiz 592, 603.
 44. Sideridou I, Tserki V, Papanastasiou G. Study of water sorption, solubility and modulus of elasticity of light-cured dimethacrylate-based dental resins. *Biomaterials* 2003;24:655-65.
 45. Schneider LF, Cavalcante LM, Pahl SA, Pfeifer CS, Ferracane JL. Curing efficiency of dental resin composites formulated with camphorquinone or trimethylbenzoyl-diphenyl-phosphine oxide. *Dent Mater* 2012;28:392-7.
 46. Santini A, Miletic V, Swift MD, Bradley M. Degree of conversion and microhardness of TPO-containing resin-based composites cured by polywave and monowave LED units. *J Dent* 2012;40:577-84.
 47. Ciccone-Nogueira JC, Borsatto MC, de Souza-Zaron WC, Ramos RP, Palma-Dibb RG. Microhardness of composite resins at different depths varying the post-irradiation time. *J Appl Oral Sci* 2007;15:305-9.

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