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Color Stability Behavior of Methacrylate-based Resin Composites Polymerized with Light-emitting Diodes and Quartz-Tungsten-Halogen

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Clinical Relevance

Ensuring optimal color match of composite restorations to the surrounding tooth structure is critical to any esthetic restorative procedure. A better understanding of the color shifts composites undergo after polymerization and storage can greatly minimize shade mismatch issues.

SUMMARY

Despite significant developments in improving the optical properties of resin composite materials, their color stability remains a challenge. This study aimed to evaluate the shade stability of light-polymerized, methacrylate-based resin composites with different filler particle composition (microfill, minifill, nanohybrids, and microhybrids) polymerized with quartz-tungsten-halogen (QTH) and light-emitting diodes (LED).

Methods and Materials: Composite discs were fabricated from Tetric EvoCeram, Premise, Artiste, and Beautifil II (nanohybrids); Filtek Supreme Plus and Vit-l-escence (microhybrids); Heliomolar (microfill); and Estelite Sigma Quick (minifill) using a Teflon mold. The specimens were irradiated either with QTH (Elipar 2500; 600 mW/cm^2) for 40 seconds or with LED (Bluephase G2; 1200 mW/cm^2) for 20 seconds. Color parameters were measured with a colorimeter before and after polymerization and at 24 hours, one week, one month, and three months. Color change was calculated among the different storage periods.

Results: There was a significant effect of the composite, time, and their interaction ($p<0.001$) but no effect of the polymerization unit on the color stability. Color changes immediately after polymerization and at 24 hours (4.22 and 3.88 for LED; and 4.08 and 3.82 for QTH) were not significantly different from each other but were both significantly higher than changes after one week (0.96 and 0.78),

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one month (1.12 and 1.02), and three months (1.27 and 1.11) for LED and QTH, respectively ($p<0.001$).

Conclusions: Color changes were observed for all the materials that were dependent on the type of composite but not on the polymerization unit. These color shifts took place primarily immediately after polymerization and after 24 hours and were additive in nature.

INTRODUCTION

Despite efforts to improve the color stability of current composite resin materials, their color remains unstable. Composite resins' optical properties are dependent on the degree of polymerization,[1,2] which is in turn a function of aspects relative to the material's composition and the amount of energy delivered on polymerization.[3-5] The type, size, amount of inorganic filler loading,[6,7] resin matrix composition,[8-12] and type and concentration of photoinitiator[13-15] as well as the wavelength of the emitted light, bulb intensity, and exposure time[16] are all known to affect the material's degree of polymerization.

Light-activated composite resins polymerize by free radical polymerization, whereby methacrylate carbon-carbon double bonds (C=C) become available for cross-linking monomers into polymeric chains.[17,18] Most light-activated systems use camphorquinone (CQ) as their photoinitiator. When exposed to blue light of wavelengths in the range of 400 to 500 nm, CQ reacts with an amine activator to form free radicals, initiating the polymerization reaction.[19] Approximately 75% of the polymerization reaction takes place during the first 10 minutes,[20,21] after which the free radicals undergo a postirradiation polymerization reaction that lasts up to 24 hours.[22] This dark polymerization can be quite extensive, with as much as 19-26% of the final monomer conversion taking place during this period.[23] However, the conversion of C=C is not complete, ranging from 55% to 75%,[21] resulting in a heterogeneous structure of densely cross-linked and poorly cross-linked areas.[24] Quartz-tungsten-halogen (QTH) and light-emitting diodes (LEDs) represent the most commonly used light-curing units (LCUs) for the polymerization of light-activated composite resins. QTH's broad emission spectrum allows polymerization of a wide range of composite materials. However, drawbacks associated with the degradation of their filters have been reported to result in inadequately polymerized restorations.[25] LEDs, with a narrower wavelength spectrum that matches more closely the absorption peak of CQ,[26] allow reduced polymerization times due to their higher irradiances.[27] In general, the same degree of conversion can be obtained with a fixed energy density, independent from variations in light irradiance and exposure time.[28] Issues derived from insufficient polymerization and residual unreacted monomers are known to compromise the polymer mechanical properties,[29,30] resulting in premature degradation, wear, and staining[9,31] as well as in a compromised color stability.[32]

The International Commission on Illumination developed the CIE L*a*b* scale, which can be used to describe the color characteristics of composite resins based on three parameters: lightness/darkness (+L*/–L*), red/green (+a*/–a*), and yellow/blue (+b*/–b*). Previous studies have demonstrated that color changes occurring in composite resins are primarily within the L* and b* parameters.[33-38] Color change is described quantitatively in delta E (ΔE^*) units, which represent the "linear distance" between two colors located in the CIE L*a*b* color space and combine changes in the L*, a*, and b* parameters. The smallest color difference that the human eye can detect has been a subject of debate. Different ΔE^* values have been proposed to determine "unacceptable" color changes with values set at $\Delta E^* \geq 2$,[39] $\Delta E^* \geq 3.3$,[10,40-42] and $\Delta E^* \geq 3.7$.[43,44]

As improved formulations of materials are developed, it is essential that studies investigate their optical properties when polymerized with different LCUs. Therefore, the aim of this study was to evaluate the polymerization-dependent color change and shade stability of eight commercially available light-polymerized, methacrylate-based composite resins with different filler particle composition (microfill, minifill, nanohybrids, and microhybrids) polymerized with QTH or LED immediately after polymerization and after different storage periods. The null hypotheses evaluated were the following: 1) There is no influence of the polymerization unit, when delivering equivalent energy densities, on the color stability of eight methacrylate-based composite resin materials. 2) There is no influence of the type of composite resin on the color stability following polymerization with an LED or QTH LCU.

METHODS AND MATERIALS

Polymerization-dependent color changes and shade stability of eight light-polymerized, methacrylate-based resin composites were evaluated in this study. The composition and energy requirements of the materials evaluated, per the manufacturers' descrip-

tions, are summarized in Table 1. Tetric EvoCeram, Premise, Artiste, and Beautifil II (nanohybrids); Filtek Supreme Plus and Vit-l-escence (microhybrids); Heliomolar (microfill); and Estelite Sigma Quick (minifill) were polymerized with either LED or QTH. Five discs, in shade A3 dentin, were fabricated for each combination of composite resin–LCU (n=5), for a total of 80 specimens, as determined by preliminary power analysis. Two LCUs were used for photoactivation of the composite resin specimens: An LED unit (Bluephase G2; Ivoclar-Vivadent, Amherst, NY, USA; 1200 mW/cm^2) and a QTH unit (Elipar 2500; 3M ESPE, St Paul, MN, USA; 600 mW/cm^2) with light probe diameters of 10 mm and 8 mm. 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 materials, referred to as radiant exposure, was calculated as the product of the irradiance and irradiation time recommended by the manufacturer. The radiant exposure values for the different materials evaluated ranged from 4.5 to 24 J/cm^2 (Table 1). For standardization of the amount of energy delivered, all specimens received 24 J/cm^2. The irradiation time was set to 20 seconds for the LED (1200 mW/cm^2×20 seconds) and 40 seconds for the QTH (600 mW/cm^2×40 seconds). The specimens were prepared by condensing the composite resin into a white polytetrafluoroethylene mold (5 mm diameter × 2 mm height) against two microscope glass slabs, with Mylar strips between the glass slabs and the mold to avoid oxygen inhibition. Glass slabs were used to provide flat specimens with a uniform surface that would be less likely to introduce variations in the color measurements.[6]

Color measurements were recorded before polymerization, immediately after polymerization, and after 24 hours, one week, one month, and three months of storage (100% humidity at 37°C) with a colorimeter (Minolta Chroma Meter model CR-321; Minolta Corp, Ramsey, NJ, USA). Calibration of the device was performed against a white calibration tile provided by the manufacturer. A measuring area of 3 mm in diameter with 45° circumferential illumination and 0° viewing angle was used. The colorimeter device measures the color of a specimen against a black background and exposed to a standard light source (D65 or regular daylight). All color measurements were recorded through the glass slabs to eliminate the potential effect of the glass specular and diffuse reflectance. Because the diameter of the colorimeter optical geometry was smaller than the diameter of the specimens, three overlapping measurements were taken and averaged to determine a single color value. Between testing periods, the specimens were stored individually in hermetically sealed containers containing distilled water in an incubator at 37°C. Color values were expressed according to the CIE L*a*b* scale color coordinates: lightness-darkness (L*), red-green (a*), and yellow-blue (b*). The overall color change (ΔE*) was calculated using the equation $\Delta E^* = [(\Delta L^*)^2 + (\Delta a^*)^2 + (\Delta b^*)^2]^{1/2}$. Mean ΔE* values were calculated between baseline and immediate polymerization, immediate polymerization and 24 hours, 24 hours and one week, one week and one month, and one month and three months. The total net color change after three months relative to baseline was also calculated. Color change values $\Delta E^* \geq 3.3$ were considered unacceptable based on thresholds designated by previous studies.[10,40-42] Further analysis of changes to the individual color parameters (ΔL*, Δa*, Δb*) was also conducted only for values $\Delta E^* \geq 3.3$.

A three-way analysis of variance (ANOVA) was used to evaluate the effect of the main variables—composite resin, time, and LCU—and their interactions on the color stability. Since no effect was detected for the variable LCU, individual two-way ANOVAs were conducted to evaluate the effect of the variables composite resin, time, and their interactions on the color stability of both LED- and QTH-polymerized samples. Post hoc Tukey tests were used for pairwise multiple comparisons of group means. For color changes above the critical threshold of 3.3, a two-way ANOVA and Tukey tests were used to evaluate the effect of the variables composite resin and LCU on each of the corresponding changes in L*, a*, and b* parameters. A significance level of $p < 0.05$ was used for all tests. All statistical analyses were performed with SigmaStat version 3.5 (San Jose, CA, USA).

RESULTS

The three-way ANOVA revealed a significant effect of the composite resin, time, and their interactions ($p<0.001$) but no effect of the LCU on the color stability (Table 2). Overall, the color change observed for specimens polymerized with LED was not significantly different from that of specimens polymerized with QTH ($p<0.162$). Individual two-way ANOVAs revealed a significant effect of the composite resin, time, and their interactions ($p<0.001$) on color stability for both LED- and QTH-polymerized samples (Table 3). Pairwise multiple comparisons revealed that color changes immediately after polymerization and at 24 hours (4.22 and 3.88 for LED, and 4.08 and 3.82 for QTH) were not significantly different from each other but were both significantly

Table 1: *Composite Resin Brands, Categories, and Composition, Per Manufacturer's Description*

Product (Manufacturer)	Lot	Category	Matrix	Photoinitiator	Energy Required,[a] (J/cm^2)
Estelite Sigma Quick (Tokuyama, Tokyo, Japan)	E674	Minifill	Bis-GMA, TEGDMA	CQ/RAP	4.5-6
Heliomolar (Ivoclar-Vivadent, Amherst, NY, USA)	M00783	Microfill	Bis-GMA, UDMA, decandiol dimethacrylate	CQ/amine	20
Tetric EvoCeram (Ivoclar-Vivadent, Amherst, NY, USA)	N58533	Nanohybrid	Dimethacrylates	CQ/amine	10
Premise (Kerr, Orange, CA, USA)	3204934	Nanohybrid	Bis-EMA, TEGDMA	CQ/amine	10
Artiste (Pentron, Wallingford, CT, USA)	167373	Nanohybrid	PCBisGMA/BisGMA/UDMA/ HDDMA	Not reported	8-12
Beautifil II (Shofu, Kyoto, Japan)	051026-51	Giomer nanohybrid	Bis-GMA, TEGDMA	CQ/amine	10
Filtek Supreme Plus (3M-ESPE, St Paul, MN, USA)	8EA	Microhybrid	Bis-GMA, Bis-EMA, UDMA, TEGDMA, PEGDMA	CQ/amine	24
Vit-l-escence (Ultradent, South Jordan, UT, USA)	B4869	Microhybrid	Bis-GMA	CQ/amine	9.2

Abbreviations: Bis-EMA, ethoxylated bisphenol A dimethacrylate; Bis-GMA, bisphenol A glycidyl dimethacrylate; CQ, camphorquinone; HDDMA, hexanediol dimethacrylate; PCBis-GMA, polycarbonate modified Bis-GMA; PEGDMA, poly (ethylene glycol) dimethacrylate; PPF, pre-polymerized filler; RAP, radical amplified photopolymerization; TEGDMA, triethylene glycol dimethacrylate; UDMA, urethane dimethacrylate.
[a] The energy requirement was calculated based on the information provided from the manufacturer regarding time and light curing unit recommended for polymerization.

higher than the changes observed after one week (0.96 and 0.78), one month (1.12 and 1.02), and three months (1.27 and 1.11) for LED and QTH ($p<0.001$), respectively. With only a few exceptions, color changes immediately after polymerization and after 24 hours surpassed the critical threshold of 3.3, and the changes after one week, one month, and three months remained below this threshold. Figure 1A and B summarizes the color changes for each material at the different testing periods for LED and QTH. The total net color changes after three months, relative to baseline, are also represented in Figure 1A and B for all the materials, which were ranked from greatest to least amount of color change as follows: Artiste (11.33) > Vit-l-escence (11.32) > Premise (10.81) > Tetric Evo Ceram (7.98) > Supreme (7.54) > Beautifil (7.51) > Estelite (4.96) > Heliomolar (4.51) for LED-polymerized specimens; and Vit-l-escence (10.56) > Premise (9.44) > Tetric Evo Ceram (7.76) > Artiste (7.36) > Beautifil (7.08) > Heliomolar (6.47) > Supreme (5.33) > Estelite (4.44) for QTH-polymerized specimens.

Subsequent analysis of the contribution of the individual parameters L*, a*, and b* to the overall color change was performed immediately after polymerization and after 24 hours only since these values exceeded the critical threshold of 3.3. Two-way ANOVA immediately after polymerization (Table 4) revealed that there was a significant effect of both composite resin and LCU on parameters ΔL^* ($p<0.001$ and $p=0.018$) and Δa^* ($p<0.001$ and

Table 2: *Three-way Analysis of Variance (ANOVA) for Color Change in Delta E (ΔE^*) Units*

Source of Variation	df	SS	MS	*F*	*P*
Composite	7	48.250	6.893	8.179	<0.001
Light	1	1.651	1.651	1.960	0.163
Time	4	841.988	210.497	249.769	<0.001
Composite × light	7	6.582	0.940	1.116	0.353
Composite × time	28	136.960	4.891	5.804	<0.001
Light × time	4	0.178	0.0445	0.0528	0.995
Composite × light × time	28	23.379	0.835	0.991	0.482
Residual	317	267.157	0.843		
Total	396	1326.172	3.349		

Abbreviations: MS, mean squares; SS, sum of squares.

Table 1: Extended.

Product (Manufacturer)	Particle Size, μm (Mean)	Filler Type	Filler content	
			%wt	%vol
Estelite Sigma Quick (Tokuyama, Tokyo, Japan)	0.1-0.3 (0.2)	Zirconia-silica, composite filler	82	71
Heliomolar (Ivoclar-Vivadent, Amherst, NY, USA)	0.04-0.2	Silicon dioxide, ytterbium trifluoride, pre-polymers	66.7	46
Tetric EvoCeram (Ivoclar-Vivadent, Amherst, NY, USA)	0.04-3.0 (0.55)	Barium glass, ytterbium trifluoride, mixed oxide, pre-polymers	75-76	53-55
Premise (Kerr, Orange, CA, USA)	PPF, 30-50; silica, 0.02; barium, 0.4	Pre-polymerized filler, barium glass, silica filler	84	70
Artiste (Pentron, Wallingford, CT, USA)	0.02-0.7	Barium boro-alumino silicate glass, nano-particulated silica, zirconium silicate	75	66
Beautifil II (Shofu, Kyoto, Japan)	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, USA)	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, USA)	0.7	Barium alumina silicate	75	58

$p<0.001$). Only the composite resin variable demonstrated a significant effect on parameter Δb* ($p<0.001$). Two-way ANOVA after 24 hours (Table 5) demonstrated that only the composite resin variable had a significant effect on parameters ΔL* ($p=0.013$) and Δa* ($p<0.001$). Neither composite resin nor LCU had an effect on parameter Δb*. The contribution of the individual parameters L*, a*, and b* to the overall color change for specimens polymerized with LED and QTH is summarized in Figure 2A and B for values obtained immediately after polymerization and in Figure 3A and B for values obtained 24 hours following polymerization.

DISCUSSION

The present study evaluated the shade stability of a number of light-polymerized methacrylate-based composite resins with different filler particle composition polymerized with QTH and LEDs. The first null hypothesis was accepted since there was no influence of the LCU on the color stability of the different materials evaluated. Although monomer conversion ratios were not determined in this study, it is possible that an equivalent degree of conversion was obtained with both LCUs, explaining, at least in part, the observed results. This is coincident with previous findings,[28] which have shown an equivalent degree of conversion with a fixed energy density, independent from variations of light irradiance and exposure time.

A wide range of color change was observed for the different materials evaluated, thus leading to rejection of the second null hypothesis. Aspects relative to the material composition, such as the type, size, amount of inorganic filler loading, resin matrix composition, and type and concentration of photoinitiator, have all been reported[14] to affect the material's degree of polymerization and may help explain the differences in color stability of the materials evaluated. Light-activated composite resins commonly use CQ/amine as their photoinitiator system. Although present in small amounts, CQ can significantly affect the material's color.[13,15] Enhanced color stability has been reported with

Table 3: *Two-way Analysis of Variance (ANOVA) for Color Change in Delta E (ΔE*) Units*

Source of Variation	LED					QTH				
	df	SS	MS	*F*	*P*	df	SS	MS	*F*	*P*
Composite	7	23.597	3.371	5.348	<0.001	7	31.111	4.444	4.228	<0.001
Time	4	413.237	103.309	163.912	<0.001	4	429.038	107.260	102.028	<0.001
Composite × time	28	73.086	2.610	4.141	<0.001	28	87.333	3.119	2.967	<0.001
Residual	157	98.953	0.630			160	168.205	1.051		
Total	196	608.240	3.103			199	715.687	3.596		

Abbreviations: MS, mean squares; SS, sum of squares.

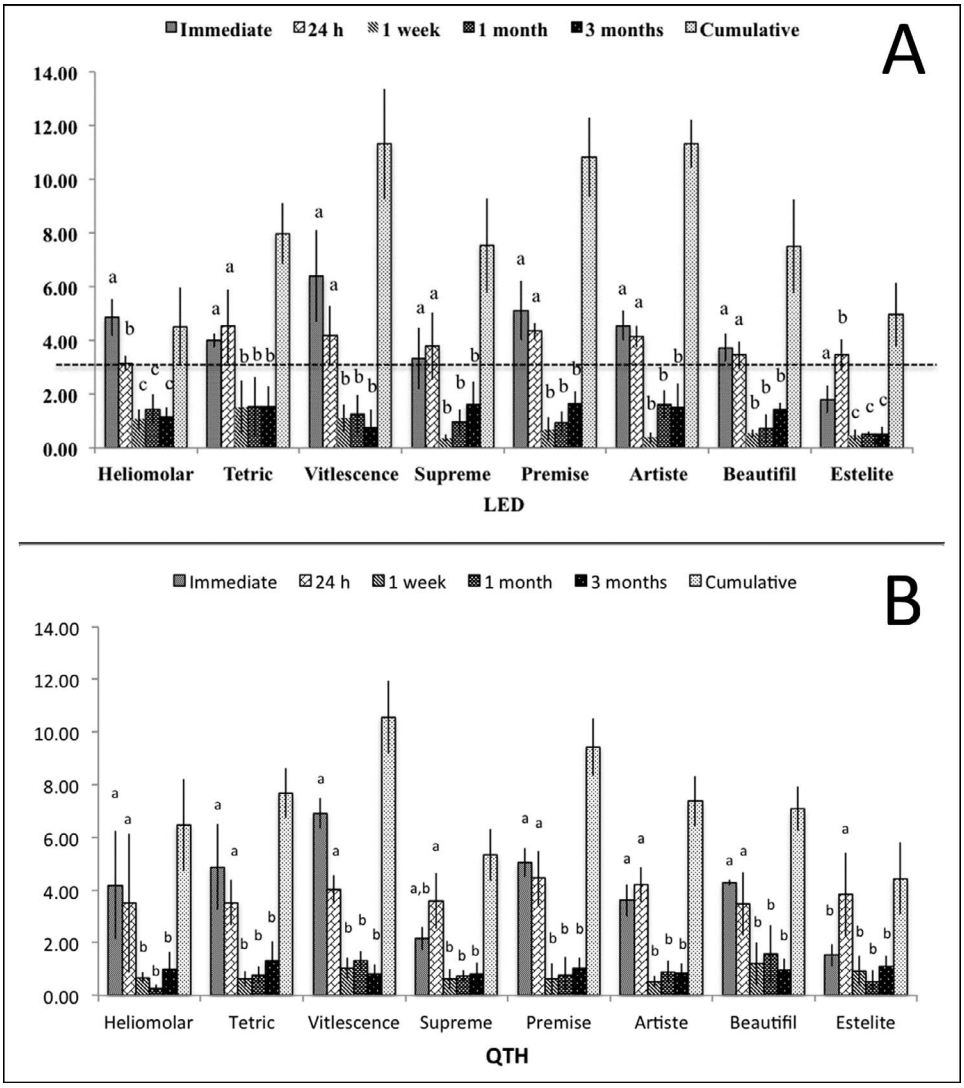

Figure 1. *(A) Mean (standard deviation [SD]) color change (ΔE*) values immediately after polymerization, at 24 hours, and after one week, one month, and three months and total net color change after three months relative to baseline for LED-polymerized specimens. Different superscript letters denote significant differences among the different 'time' intervals within each composite resin group (Tukey test,* $p<0.05$*). (B) Mean (SD) ΔE* values immediately after polymerization, at 24 hours, and after one week, one month, and three months and total net color change after three months relative to baseline for QTH-polymerized specimens. Different superscript letters denote significant differences among the different 'time' intervals within each composite resin group (Tukey test,* $p<0.05$*).*

Table 4: *Two-way Analysis of Variance (ANOVA) for ΔL*, Δa*, and Δb* Immediately After Polymerization*

Source of Variation	df	ΔL*				Δa*				Δb*			
		SS	MS	F	P	SS	MS	F	P	SS	MS	F	P
Composite	7	384.800	54.971	63.066	<0.001	16.111	2.302	16.128	<0.001	86.901	12.414	10.683	<0.001
Light	1	5.126	5.126	5.881	0.018	2.702	2.702	18.933	<0.001	0.615	0.615	0.530	0.469
Composite × light	7	12.170	1.739	1.995	0.069	1.852	0.265	1.854	0.092	15.355	2.194	1.888	0.086
Residual	65	56.657	0.872			9.276	0.143			75.536	1.162		
Total	80	465.015	5.813			29.767	0.372			178.446	2.231		

Abbreviations: MS, mean squares; SS, sum of squares.

Table 5: *Two-way Analysis of Variance (ANOVA) for ΔL*, Δa*, and Δb* After 24 Hours*

Source of Variation	df	ΔL*				Δa*				Δb*			
		SS	MS	*F*	*P*	SS	MS	*F*	*P*	SS	MS	*F*	*P*
Composite	7	17.964	2.566	2.803	0.013	2.146	0.307	10.401	<0.001	15.691	2.242	1.532	0.173
Light	1	2.032	2.032	2.220	0.141	0.0162	0.0162	0.551	0.461	2.574	2.574	1.759	0.189
Composite × light	7	4.449	0.636	0.694	0.677	0.516	0.0737	2.500	0.025	9.613	1.373	0.938	0.484
Residual	64	58.590	0.915			1.886	0.0295			93.662	1.463		
Total	79	83.034	1.051			4.564	0.0578			121.540	1.538		

Abbreviations: MS, mean squares; SS, sum of squares.

increased filler loading[6,7] and less resin volume fraction.[10,11] The nature of the matrix is also known to affect the color stability of composite resins with more hydrophilic monomers, resulting in greater water absorption and thus greater color change,[8] and with more hydrophobic monomers resulting in less water sorption and enhanced color stability.[8-10] The amount of triethylene glycol dimethacrylate (TEGDMA) present in the resin matrix has also been reported to affect the extent of postirradiation polymerization. [12] As TEGDMA increases, the amount of postirradiation polymerization decreases

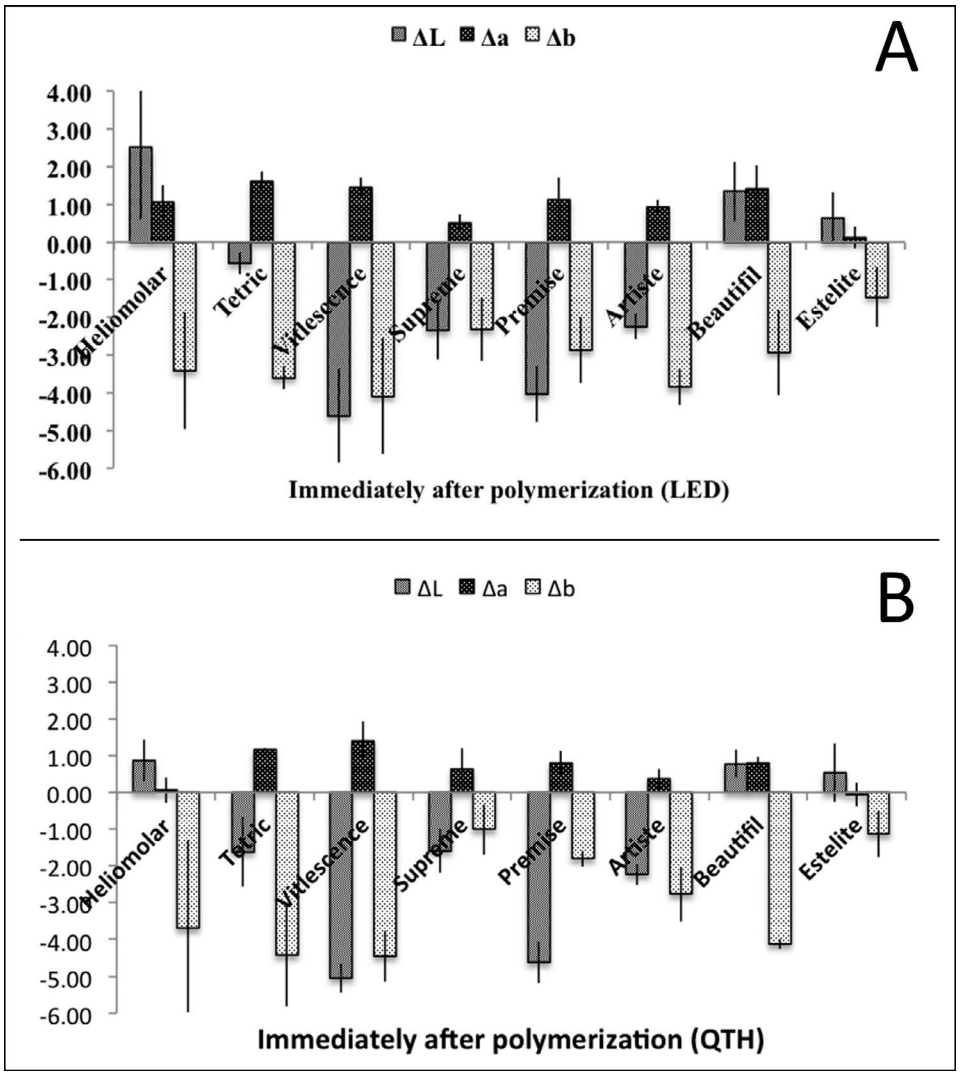

Figure 2. *(A) Mean change on ΔL*, Δa*, and Δb* parameters immediately after polymerization for LED-polymerized specimens. (B) Mean change on ΔL*, Δa*, and Δb* parameters immediately after polymerization for QTH-polymerized specimens.*

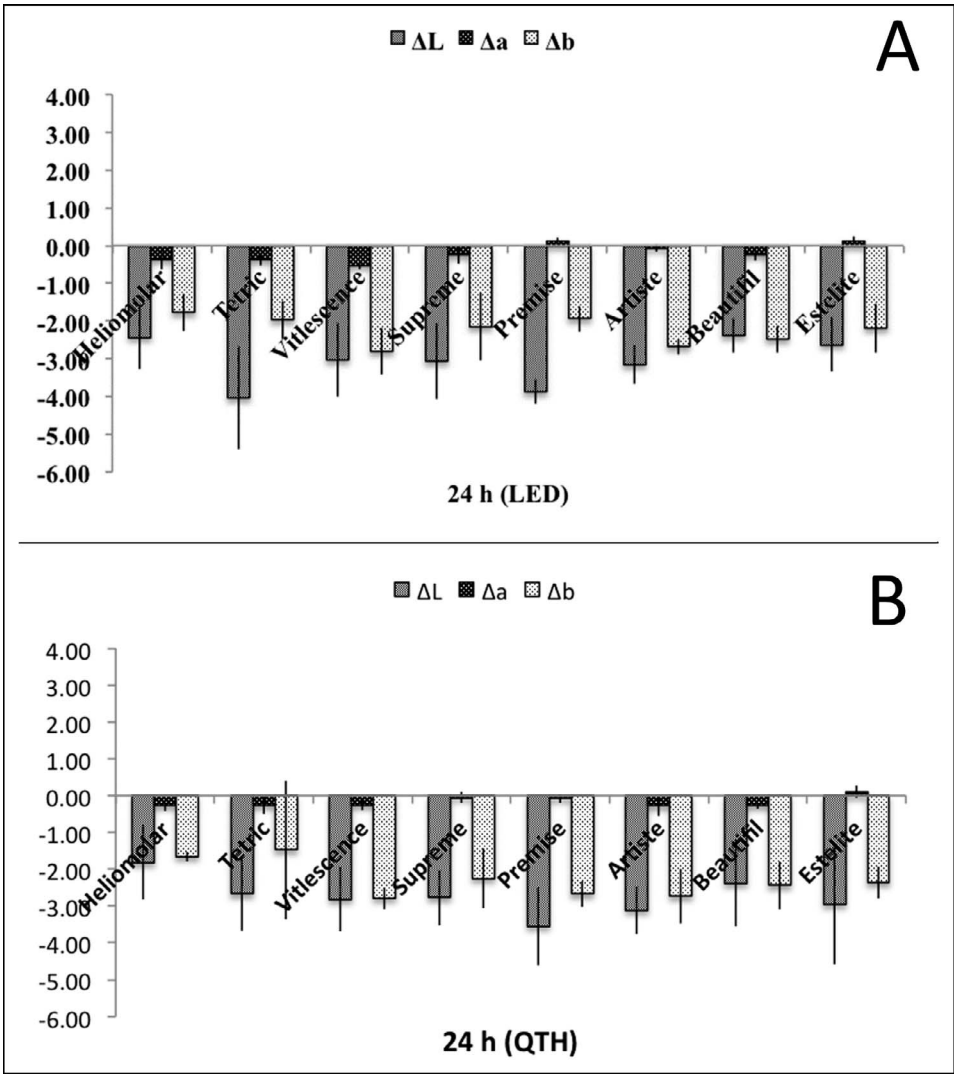

Figure 3. *(A) Mean change on ΔL*, Δa*, and Δb* parameters 24 hours following polymerization for LED-polymerized specimens. (B) Mean change on ΔL*, Δa*, and Δb* parameters 24 hours following polymerization for QTH-polymerized specimens.*

because TEGDMA generates higher initial conversion. However, correlations between the amount of color change and TEGDMA content cannot be established, since detailed compositional information of these materials is proprietary.

The color change of materials with different compositions was followed between storage periods to evaluate behavioral patterns inherent in each material. A common trend was observed, whereby all materials exhibited large color shifts immediately after polymerization and 24 hours following polymerization, but changes at subsequent intervals were negligible, indicating that they only played a minor role in the total net color change result after three months. For most materials, the degree of polymerization on initial light irradiation and 24 hours following irradiation with light was enough to generate clinically relevant color shifts above the threshold of 3.3 (Figure 1A,B). Polymerization-dependent color changes can be attributed to shifts in the resin optical properties, which take place during cross-linking of the monomers into polymeric chains.[17] The degree of polymerization is in turn dependent on factors such as the radiant intensity of the polymerization unit and polymerization time.[3,4] To standardize the amount of energy delivered to the different materials, all specimens received 24 J/cm^2. Although monomer conversion ratios were not calculated as a part of this study, it is possible that the degree of polymerization may have been maximized for materials such as Estelite Sigma, which received 24 J/cm^2 despite the recommended manufacturer energy requirement of 4.5-6 J/cm^2, perhaps leading to an enhanced color stability relative to

other brands. Clinically, a color mock-up is indicated for shade selection to account for color changes that may take place during polymerization. Changes taking place 24 hours following polymerization are even more critical to understand, as accurate predictions of these changes can significantly help minimize the shade discrepancies that may occur during this postirradiation polymerization reaction. Under the testing conditions evaluated in this study, color changes after one week, one month, and three months could be attributed to the aging conditions, such as water absorption and polymer swelling, which are in turn a function of the initial extent of polymerization of the material.[2] The negligible color changes observed at these testing intervals are suggestive of an improved chemistry of contemporary composite resin materials and indicate that, provided that an accurate color match has been obtained after 24 hours of placement, shade discrepancies after some time of intraoral function may be attributed to extrinsic factors.

The total net color change after three months, relative to baseline, was also unacceptable for all the composite materials evaluated, as it surpassed the threshold of 3.3 (Figure 1A,B). Materials with the largest net color change, Artiste (11.33), Vit-l-escence (11.32), and Premise (10.81) polymerized with LED; and Vit-l-escence (10.56) and Premise (9.44) polymerized with QTH, can be explained by the additive nature of the changes that took place immediately after polymerization and after 24 hours (Figures 2A,B and 3A,B). Vit-l-escence and Premise are heavily filled materials and use CQ/amine as their photoinitiator system. Estelite Sigma Quick, which showed the least color change of all materials, is also heavily filled, but it uses a radical amplified photo-polymerization system as the catalyst to initiate the setting reaction, allowing less CQ to be used, explaining, at least partially, its improved color stability relative to other materials.

More in-depth information regarding the behavior of the different materials was derived from an analysis of the contribution of the individual parameters L*, a*, and b* to the overall color change. This evaluation was conducted immediately after polymerization and after 24 hours, since these were the only values that exceeded the critical threshold of 3.3, and hence were considered the main changes responsible for total net color change after three months, relative to baseline. Parameters L* and b* were responsible for most of the observed changes, whereas changes to the a* parameter were negligible. Coincident with our results, previous studies have reported the a* parameter to contribute the least to the overall color change.[33-35] Analysis of the individual L*, a*, and b* parameters immediately after polymerization (Figure 2A,B) revealed similar behavior for most materials. The color change was derived predominantly from shifts to the dark (−L) and blue (−b) region. The only exceptions were Heliomolar, Beautifil, and Estelite, which shifted to the light (+L) rather than the dark (−L) region. Changes to the a* parameter were considerably smaller and almost always directed to the red (+a) region. After 24 hours (Figure 3A,B), all materials displayed the same behavior. Color shifts were primarily derived from shifts to the dark (−L) and blue (−b) region, the same direction as the changes immediately after polymerization, indicating that these changes were additive in nature, rather than neutralizing each other, as demonstrated in a previous study.[35] Changes to the a* parameter were negligible and, in most cases, neutralized the changes immediately after polymerization, since they were directed to the green (−a) region. To an extent, immediate and 24-hour changes to the L* parameter for Heliomolar, Beautifil, and Estelite neutralized each other, since these shifts took place in opposite directions but were not exactly of the same extent. Based on the additive nature of the color shifts observed immediately after polymerization and after 24 hours, and the relatively minor changes under the threshold of 3.3 observed at subsequent time intervals, it is safe to conclude that the total net color change result after three months was primarily derived from changes to the dark and blue region, which took place primarily immediately after polymerization and 24 hours following polymerization. This is in agreement with results from previous studies, which have shown a decrease in the L*[6,36,37] and b* [6,13,37,38] coordinates after polymerization, regardless of the brand and shade. Materials that use CQ as photoinitiator are known to become less yellow as the photoinitiator is consumed.[13] However, no estimations can be made based solely on the compositional information, since manufacturers do not typically disclose the amount of CQ.

Newer formulations of composite resin materials offer great potential provided their color stability behavior is understood. The present study aimed to investigate intrinsic material- and polymerization-dependent factors, which may affect the color stability of materials with different composition, by providing an in-depth analysis of the extent and nature of the color shifts taking place during initial setting and storage. By gaining a better understanding of the changes taking place at the different

stages in the maturation process, behavioral trends inherent to specific materials can be established, allowing clinicians to make more accurate predictions regarding the direction and magnitude of the changes expected to take place. A better understanding of the material of their choice is critical to assisting clinicians to minimize shade mismatching issues, thereby improving the long-term esthetic results of their restorations. Once reproducible behavioral trends for specific materials have been established, further research should investigate the behavior of the different materials when they are exposed to various staining solutions over longer incubation periods. Moreover, future color stability studies should be conducted in a clinical setting using intraoral color measurement devices and following the thresholds of color perceptibility (ΔE^* of 2.6) and acceptability (ΔE^* of 5.5) established by Douglas and others.[45] Similar to other *in vitro* studies, our study reported color stability of monochromatic composite samples taken benchtop under perfect lighting conditions. A threshold of 3.3 was used to indicate unacceptable color changes, as determined by previous studies.[41] This threshold is applicable to laboratory conditions such as those described above and cannot be extrapolated as a threshold for "clinical unacceptability."

CONCLUSIONS

Within the limitations of this *in vitro* study, it can be concluded that when delivering equivalent energy densities, polymerization with LED or QTH did not have a significant influence on the color change. A significant effect of the type of composite resin on the color change was shown regardless of the LCU. The overall color shift after three months was primarily derived from changes to the dark and blue regions, which took place immediately after polymerization and after 24 hours. These changes were additive in nature. Color changes after one week, one month, and three months were negligible, and thus their contribution to the total net color change after three months was considered minor.

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Note

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Conflict of Interest

The Authors of this manuscript certify that they have no proprietary, financial or other personal interest of any nature or kind in any product, service and/or company that is presented in this article.

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REFERENCES

1. Tseng WY, Huang CH, Chen RS, Lee MS, Chen YJ, Rueggeberg FA, & Chen MH (2007) Monomer conversion and cytotoxicity of dental composites irradiated with different modes of photoactivated curing *Journal of Biomedical Materials Research Part B Applied Biomaterials* **83(1)** 85-90.
2. Ferracane JL (2006) Hygroscopic and hydrolytic effects in dental polymer networks *Dental Materials* **22(3)** 211-222.
3. Arikawa H, Kanie T, Fujii K, Takahashi H, & Ban S (2007) Effect of filler properties in composite resins on light transmittance characteristics and color *Dental Materials Journal* **26(1)** 38-44.
4. Emami N, Sjodahl M, & Soderholm KJM (2005) How filler properties, filter fraction, sample thickness and light source affect light attenuation in particulate filled resin composites *Dental Materials* **21(8)** 721-730.
5. Falkensammer F, Arnetzl GV, Wildburger A, & Freudenthaler J (2013) Color stability of different composite resin materials *Journal of Prosthetic Dentistry* **109(6)** 378-383.
6. Eldiwany M, Friedl KH, & Powers JM (1995) Color stability of light-cured and post-cured composites *American Journal of Dentistry* **8(4)** 179-181.
7. Schulze KA, Marshall SJ, Gansky SA, & Marshall GW (2003) Color stability and hardness in dental composites after accelerated aging *Dental Materials* **19(7)** 612-619.
8. Buchalla W, Attin T, Hilgers RD, & Hellwig E (2002) The effect of water storage and light exposure on the color and translucency of a hybrid and a microfilled composite *Journal of Prosthetic Dentistry* **87(3)** 264-270.
9. Dietschi D, Campanile G, Holz J, & Meyer JM (1994) Comparison of the color stability of ten new-generation composites—An in-vitro study *Dental Materials* **10(5-6)** 353-362.
10. Inokoshi S, Burrow MF, Kataumi M, Yamada T, & Takatsu T (1996) Opacity and color changes of tooth-colored restorative materials *Operative Dentistry* **21(2)** 73-80.
11. Reis AF, Giannini M, Lovadino JR, & Ambrosano GM (2003) Effects of various finishing systems on the surface roughness and staining susceptibility of packable composite resins *Dental Materials* **19(1)** 12-18.
12. Tarumi H, Imazato S, Ehara A, Kato S, Ebi N, & Ebisu S (1999) Post-irradiation polymerization of composites containing bis-GMA and TEGDMA *Dental Materials* **15(4)** 238-242.
13. Janda R, Roulet JF, Kaminsky M, Steffin G, & Latta M (2004) Color stability of resin matrix restorative materials as a function of the method of light activation *European Journal of Oral Sciences* **112(3)** 280-285.

14. Leonard DL, Charlton DG, Roberts HW, & Cohen ME (2002) Polymerization efficiency of LED curing lights *Journal of Esthetic and Restorative Dentistry* **14(5)** 286-295.
15. Shin DH, & Rawls HR (2009) Degree of conversion and color stability of the light curing resin with new photo-initiator systems *Dental Materials* **25(8)** 1030-1038.
16. Aravamudhan K, Rakowski D, & Fan PL (2006) Variation of depth of cure and intensity with distance using LED curing lights *Dental Materials* **22(11)** 988-994.
17. Lee YK, & Powers JM (2001) Color and optical properties of resin-based composites for bleached teeth after polymerization and accelerated aging *American Journal of Dentistry* **14(6)** 349-354.
18. Peutzfeldt A (1997) Resin composites in dentistry: The monomer systems *European Journal of Oral Sciences* **105(2)** 97-116.
19. Rueggeberg F (1999) Contemporary issues in photocuring *Compendum of Continuing Education in Dentistry Supplement* **(25)** S4-S15.
20. 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.
21. Ferracane JL, & Greener EH (1986) The effect of resin formulation on the degree of conversion and mechanical properties of dental restorative resins *Journal of Biomedical Materials Research* **20(1)** 121-131.
22. Eliades GC, Vougiouklakis GJ, & Caputo AA (1987) Degree of double bond conversion in light-cured composites *Dental Materials* **3(1)** 19-25.
23. Halvorson RH, Erickson RL, & Davidson CL (2002) Energy dependent polymerization of resin-based composite *Dental Materials* **18(6)** 463-469.
24. Sideridou I, Tserki V, & Papanastasiou G (2002) Effect of chemical structure on degree of conversion in light-cured dimethacrylate-based dental resins *Biomaterials* **23(8)** 1819-1829.
25. Mills RW, Uhl A, Blackwell GB, & Jandt KD (2002) High power light emitting diode (LED) arrays versus halogen light polymerization of oral biomaterials: Barcol hardness, compressive strength and radiometric properties *Biomaterials* **23(14)** 2955-2963.
26. Uhl A, Sigusch BW, & Jandt KD (2004) Second generation LEDs for the polymerization of oral biomaterials *Dental Materials* **20(1)** 80-87.
27. Fleming GJ, Awan M, Cooper PR, & Sloan AJ (2008) The potential of a resin-composite to be cured to a 4mm depth *Dental Materials* **24(4)** 522-529.
28. Emami N, & Soderholm KJ (2003) How light irradiance and curing time affect monomer conversion in light-cured resin composites *European Journal of Oral Sciences* **111(6)** 536-542.
29. 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.
30. Mills RW, Jandt KD, & Ashworth SH (1999) Dental composite depth of cure with halogen and blue light emitting diode technology *British Dental Journal* **186(8)** 388-391.
31. Doray PG, Wang X, Powers JM, & Burgess JO (1997) Accelerated aging affects color stability of provisional restorative materials *Journal of Prosthodontics* **6(3)** 183-188.
32. Micali B, & Basting RT (2004) Effectiveness of composite resin polymerization using light-emitting diodes (LEDs) or halogen-based light-curing units *Brazilian Journal of Oral Research* **18(3)** 266-270.
33. Janda R, Roulet JF, Latta M, Steffin G, & Ruttermann S (2005) Color stability of resin-based filling materials after aging when cured with plasma or halogen light *European Journal of Oral Sciences* **113(3)** 251-257.
34. Kim IJ, & Lee YK (2007) Changes in color and color parameters of dental resin composites after polymerization *Journal of Biomedical Materials Research Part B Applied Biomaterials* **80B(2)** 541-546.
35. Sabatini C, Campillo M, & Aref J (2012) Color stability of ten resin-based restorative materials *Journal of Esthetic and Restorative Dentistry* **24(3)** 185-199.
36. Paravina RD, Ontiveros JC, & Powers JM (2002) Curing-dependent changes in color and translucency parameter of composite bleach shades *Journal of Esthetic and Restorative Dentistry* **14(3)** 158-166.
37. Seghi RR, Gritz MD, & Kim J (1990) Colorimetric changes in composites resulting from visible-light-initiated polymerization *Dental Materials* **6(2)** 133-137.
38. Sidhu SK, Ikeda T, Omata Y, Fujita M, & Sano H (2006) Change of color and translucency by light curing in resin composites *Operative Dentistry* **31(5)** 598-603.
39. O'Brien WJ, Groh CL, & Boenke KM (1990) A new, small-color-difference equation for dental shades *Journal of Dental Research* **69(11)** 1762-1764.
40. Kim HS, & Um CM (1996) Color differences between resin composites and shade guides *Quintessence International* **27(8)** 559-567.
41. Ruyter IE, Nilner K, & Moller B (1987) Color stability of dental composite resin materials for crown and bridge veneers *Dental Materials* **3(5)** 246-251.
42. Vichi A, Ferrari M, & Davidson CL (2004) Color and opacity variations in three different resin-based composite products after water aging *Dental Materials* **20(6)** 530-534.
43. Kim BJ, & Lee YK (2009) Influence of the shade designation on the color difference between the same shade-designated resin composites by the brand *Dental Materials* **25(9)** 1148-1154.
44. Paravina RD, Kimura M, & Powers JM (2005) Evaluation of polymerization-dependent changes in color and translucency of resin composites using two formulae *Odontology* **93(1)** 46-51.
45. Douglas RD, Steinhauer TJ, & Wee AG (2007) Intraoral determination of the tolerance of dentists for perceptibility and acceptability of shade mismatch *Journal of Prosthetic Dentistry* **97(4)** 200-208.