Clin Oral Invest (2010) 14:599–605
DOI 10.1007/s00784-009-0316-y

ORIGINAL ARTICLE

Effect of exposure time on the color stability of resin-based restorative materials when polymerized with quartz–tungsten halogen and LED light

Stefan Rüttermann · Kim Suyoun · Wolfgang H.-M. Raab · Ralf Janda

Received: 2 March 2009 / Accepted: 6 July 2009 / Published online: 21 July 2009

Abstract The objective of this study was to investigate the effect of exposure time on color stability of resin-based restorative materials when polymerized with quartz–tungsten halogen light (QTH) or light-emitting diode light (LED). Eight samples of Ceram-X Mono, Dyract eXtra, and Tetric EvoCeram each were cured for 10, 20, and 60 s with QTH or LED. The CIE-Lab values (L^*, a^*, b^*) were measured prior to and after performing water storage or a Suntest, and ΔL, Δa, Δb, and ΔE were calculated. Statistical analysis ($p<$ 0.05) showed significant changes of the color values after each of the aging processes as well as between ΔL, Δa, Δb, and ΔE of the materials in dependence of the curing device, exposure time, aging condition, and material formulation. LED performed similarly or even better with 10-s exposure time than QTH with 20 s. No improvement of color stability was achieved with increasing exposure time of 60 s either for LED or for QTH. Exposure time, emission spectrum of the light-curing device, as well as the individual material formulation influence color stability. There is apparently an exposure time above which the individual material formulation, especially type and amount of photoinitiator or synergist, dominate the color stability.

Keywords Resin-based restorative material · Exposure time · Quartz–tungsten halogen light polymerization · LED-light polymerization · Color stability · QTH

Results are part of the thesis of Suyoun Kim.

S. Rüttermann · K. Suyoun · W. H.-M. Raab · R. Janda (✉)
Medical Faculty, Centre of Dentistry,
Department of Operative and Preventive Dentistry
and Endodontics, Heinrich-Heine-University,
Moorenstr. 5, Geb. 18.13,
40225 Düsseldorf, Germany
e-mail: Ralf.Janda@uni-duesseldorf.de

Introduction

Light-emitting diode (LED) curing lights are increasingly used to polymerize resin-based restorative materials, and their effect on the physical properties of resin-based restorative materials has been investigated [1–7]. Since contemporary LED lights provide superior irradiance (approximately 1,000 mW cm^{-2}) to quartz–tungsten halogen light (QTH; approximately 800 mW cm^{-2}), LED lights are expected to optimally polymerize resin materials as or even more effective than QTH [1, 3, 8, 9]. While there are many publications discussing the physical properties of LED-light-cured materials, there are few that investigated the color stability of resin-based restorative materials when cured with quartz–tungsten halogen and LED lights [10, 11] or with plasma lights [12, 13]. These publications report that color stability not only depended on the materials' individual formulations but also on the curing time and curing device. However, none of the cited literature directly compared the color stability of QTH-light-cured with LED-light-cured materials. Since color stability is an essential clinical factor for modern restorative materials, the present work considered this property in terms of different exposure times applied on an ormocer, compomer, and microhybrid.

The goal of the present investigation was to determine the effect of QTH or LED light polymerization on the color stability of contemporary resin-based restorative materials as a function of exposure time. Since $\Delta E \geq 1$ was evaluated to be clinically perceptible and $\Delta E \geq 3$ to be unacceptable [14, 15], significant differences between each of the ΔE values and the limits of ΔE=1 and ΔE=3 were considered too. The null hypothesis was that there is no difference in color stability when polymerization is done for the same time periods with LED or QTH.

Materials and methods

Several types of contemporary light-cured, resin-based restorative material were chosen (Table 1) to investigate whether the composition influenced the results. The LED light bluephase (10-mm diameter standard light tip, Ivoclar Vivadent AG, Schaan, Liechtenstein) and the quartz–tungsten halogen light Hilux Ultra Plus (11-mm diameter standard light guide, Benlioglu Dental Inc. Ankara, Turkey) were used for polymerization. According to the manufacturers' technical information, bluephase emits light between 430 and 490 nm and Hilux Ultra Plus between 390 and 510 nm. The photometer (Curing Light Meter, Benlioglu Dental Inc., Ankara, Turkey) measured a maximum irradiance of 900±10 mW cm^{-2} for bluephase and 800±60 mW cm^{-2} for Hilux Ultra Plus when the light guide was placed directly on the sensor (diameter approximately 12 mm). The irradiance was checked each time after every series of eight specimens was cured.

From each test material, six groups of 16 specimens each (thickness, 1±0.1 mm; diameter, 10±0.1 mm), 288 specimens in total (Fig. 1), were prepared. Both sides of the specimens were covered by a 0.05 mm transparent polyester film to avoid an inhibition layer. Group 1 was QTH-irradiated for 10 s, group 2 for 20 s, and group 3 for 60 s. Groups 4, 5, and 6 were LED-light-irradiated accordingly. The specimens were polymerized in one step and from one side only by fixing the light guide or tip on a support at a distance of exactly 5 mm from the surface to ensure that they were completely irradiated. From this distance, the irradiance of bluephase was reduced by 12% and of Hilux Ultra Plus by 15%. Therefore, the actual irradiance to cure the materials was 790±11 mW cm^{-2} for bluephase and 704±45 mW cm^{-2} for Hilux Ultra Plus. Thus, the radiation doses were 8 J cm^{-2} for 10 s, 16 J cm^{-2} for 20 s, and 47 J cm^{-2} for 60 s for bluephase as well as 7 J cm^{-2} for 10 s, 14 J cm^{-2} for 20 s, and 42 J cm^{-2} for 60-s curing time for Hilux Ultra Plus.

One half of each group was stored in water at 37°C and the other half was Suntest-treated (irradiation with xenon arc lamp, 150,000 lx, wavelength > 370 nm, 24 h in water at 37°C) according to EN ISO 7491 (Suntest CPS+, Atlas Material Testing Technology GmbH, Linsengericht, Germany) followed by additional water storage at 37°C (Fig. 1). The L^*, a^*, and b^* values (L^* = lightness, $+a^*$ = red, $-a^*$ = green, $+b^*$ = yellow, $-b^*$ = blue) were measured prior to and after aging to calculate ΔL, Δa, Δb, as well as ΔE ($\Delta E = \sqrt{(\Delta L^2 + \Delta a^2 + {}^{\sim}\Delta b^2)}$). Color measurements were made the first time after 90 min of dry and dark storage to obtain the color values at the earliest possible time, since color changes may occur even after 1 day of dry and dark storage [10, 12]. The water-stored groups were measured 24 h and 180 days later, and the Suntest-treated groups were measured 2 h after finishing the Suntest and again after 180 days water storage at 37°C.

Table 1 Test materials

Material	Formulation	Manufacturer
Ceram-X Mono[a], shade: A3 microhybrid composite with partial silicium–organically modified resin matrix (Ormocer) lot: 0507001097	Resin matrix: methacrylate modified polysiloxane, dimethacrylate resin, inorganic filler: silaned Ba–Al–borosilicate glass (1.1–1. 5 µm), silaned pyrogenic SiO_2, filler content: 76 wt.%, 57 vol.%, photoinitiator: camphorquinone, synergist: ethyl-4-(*N*,*N*-dimethylamino) benzoate, UV stabilizer, stabilizer: butylated hydroxy toluene	DeTrey Dentsply GmbH, Constance, Germany
Dyract eXtra[b], shade: A3 TCB resin matrix modified fluorosilacate glass containing composite (Compomer) Lot: 0508000375	Resin matrix: ethoxylated Bisphenol-A-dimethacrylate, urethane resin, TEGDMA, TMPTMA, TCB-resin, inorganic filler: silaned strontium fluoride glass (approximately 0.8 µm), filler content: .approximately 50 vol.%, photoinitiator: camphoroquinone, synergist: ethyl-4-(dimethylamino) benzoate	DeTrey Dentsply GmbH
Tetric EvoCeram[c], shade: A3.5 (no A3 available) microhybrid Lot: H12054	Resin matrix: UDMA, Bis-GMA, ethoxylated Bis-EDMA, inorganic filler: silaned Ba-Al-borosilicate glass, Al_2O_3, Yb_3, pyrogenic SiO_2, filler content: approximately 48.5 wt.%. pre-polymer filled with pyrogenic SiO_2, filler content: approximately 34 wt.%, total filler content: approximately 60 vol.%, photoinitiator: camphorquinone, diphenyl(2,4,6-trimethybenzoyl)-phosphine oxide, synergist: tertiary amine	Ivoclar Vivadent AG, Schaan, Liechtenstein

Bis-GMA bisphenol-A-dimethacrylate, *UDMA* urethane dimethacrylate, *TEGDMA* triethyleneglycol dimetacrylate, *TMPTMA* trimethylolpropane trimethacrylate, *TCB resin* tetracarboxylic acid hydroxyethyl methacrylate ester

[a] [21–24]

[b] [31, 32]

[c] [7, 33, 34]

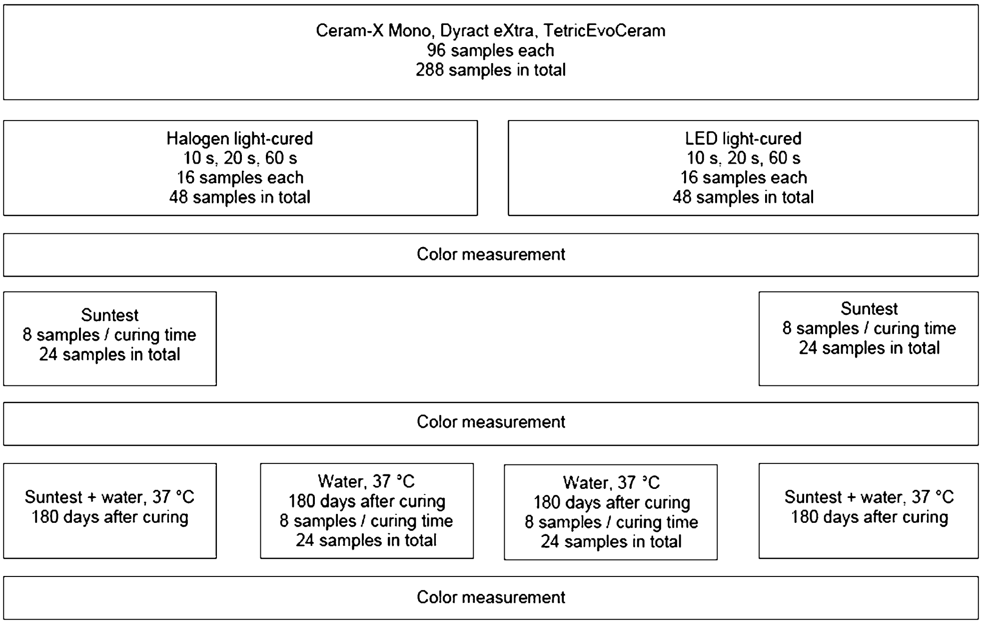

Fig. 1 Experimental design

The specimens were blot-dried and color was measured from the irradiated side (X-Rite SP62 spectrophotometer, X-Rite GmbH, Cologne, Germany). Each specimen was centered in front of a 4 mm diameter opening of the integrated Ulbricht sphere. The background was the white standard ("ideal" white tile) in direct contact with the specimen.

Statistical analysis

Statistical analysis was conducted with SPSS software 15.0 (SPSS Inc., Chicago, IL, USA). Means and standard deviations were calculated. Normal distribution was tested by the Kolmogoroff–Smirnoff test. Since the same specimens were used, repeated measures analysis of variance (ANOVA) was applied to reveal significant differences of L^*, a^*, and b^* prior to and after aging for each material, exposure time, and curing device. Multivariate ANOVA analyzed the influence of the independent variables curing device, material, exposure time, and aging on ΔL, Δa, Δb, and ΔE. Multiple comparisons of ΔL, Δa, Δb, and ΔE between the curing devices and exposure times after the different aging conditions were done with the multivariate ANOVA followed by a Bonferroni's post hoc test. The repeated application of the paired t test identified significant differences between ΔE of the 24-h and 180-day storage periods of the respective sample groups. Significant deviations of each ΔE from limit value 1 or limit value 3 were calculated with the lowest significant difference ANOVA. Statistical significance was $p<0.05$ for all tests.

Results

The results are shown in Tables 2 and 3. Changes of the L^*, a^*, and b^* values below 1 are not considered to be of clinical relevance [10, 12, 14]. The repeated measures ANOVA showed significant changes of L^*, a^*, and b^* values for each light-curing device, material, and curing time after aging (Tables 2 and 3). Multivariate ANOVA and Bonferroni's post hoc test revealed differences between the ΔL, Δa, Δb, and ΔE values of the materials that were dependent on the curing device, exposure time, and aging condition (Tables 2 and 3).

$\Delta E \geq 1$ was found after water storage for all QTH-light-cured materials, but not for Ceram-X Mono and Tetric EvoCeram LED-light-cured samples (Table 2). After finishing the Suntest, Ceram-X Mono and Dyract eXtra exceeded $\Delta E \geq 1$ for some exposure times, whereas Tetric EvoCeram did so for all (Table 3). Dyract eXtra and Tetric EvoCeram even showed $\Delta E \geq 3$ after the subsequent water storage for some exposure times independent of the curing device (Table 3). After the Suntest and the subsequent water storage, significant increases of ΔE were observed for Dyract eXtra cured for 10 and 60 s and Tetric EvoCeram samples cured for 10 and 20 s with the QTH or LED light.

After the Suntest, the materials and the curing devices significantly differed in ΔL, Δa, and Δb, but the exposure times differed in ΔL and Δb. After 180 days of storage solely in water or after the Suntest and the subsequent water storage, multivariate ANOVA revealed significant differences of ΔL, Δa, and Δb between the materials and of Δa and Δb between the exposure times and aging methods.

Table 2 Means and (standard deviations) after 180 days of water storage

	Ceram X Mono						Dyract eXtra						Tetric EvoCeram					
	Halogen			LED			Halogen			LED			Halogen			LED		
	10s	20s	60s	10s	20s	60s	10s	20s	60s	10s	20s	60s	10s	20s	60s	10s	20s	60s
Initial values - Storage: 90 min. dry. room temperature. dark																		
L*	74.1 (0.8)	74.4 (0.8)	75.8 (0.9)	72.7 (0.5)	73.4 (1.4)	73.0 (0.8)	71.8 (1.0)	72.3 (0.7)	72.6 (1.1)	71.6 (1.1)	71.7 (0.5)	72.6 (0.4)	73.3 (0.5)	72.9 (0.6)	73.2 (0.7)	71.5 (1.3)	72.6 (1.2)	72.0 (1.0)
a*	3.6 (0.1)	3.5 (0.2)	3.7 (0.1)	3.9 (0.2)	3.7 (0.1)	3.7 (0.3)	3.9 (0.3)	4.3 (0.2)	4.3 (0.3)	4.3 (0.3)	4.3 (0.2)	4.2 (0.2)	7.2 (0.3)	7.0 (0.2)	7.1 (0.2)	7.1 (0.2)	7.4 (0.3)	7.6 (0.3)
b*	23.9 (0.7)	21.5 (1.0)	19.8 (0.4)	25.0 (0.8)	23.5 (0.4)	21.5 (1.1)	23.2 (1.0)	23.2 (1.0)	19.8 (1.2)	22.4 (0.7)	21.0 (1.2)	19.7 (0.5)	29.9 (0.8)	28.7 (0.5)	26.4 (0.6)	30.4 (0.7)	30.1 (0.9)	30.0 (1.3)
Change of initial values - Storage: 180 d, water 37 °C. dark																		
ΔL	***-1.2$_{1}$ (0.4)***	***-1.0$_{2}$ (0.5)***	***-2.3$_{12}$ (0.4)***	0.4 (0.3)	-0.8 (1.2)	0.1 (0.6)	***1.0 (0.7)***	0.3 (0.4)	0.3 (0.8)	0.4 (0.4)	***0.9 (0.4)***	0.6 (0.9)	-0.8 (0.8)	***-1.2 (0.6)***	***-0.9 (0.6)***	***0.8 (0.4)***	***1.0 (0.6)***	***1.5 (0.5)***
Δa	***0.9 (0.1)***	***0.9 (0.2)***	***0.6 (0.1)***	***0.6 (0.2)***	***0.7 (0.1)***	***0.5 (0.2)***	***1.1$_{1}$ (0.2)***	***0.7 (0.2)***	***0.5$_{1}$ (0.1)***	***0.7 (0.2)***	0.4 (0.4)	***0.6 (0.3)***	***0.9 (0.3)***	***1.3 (0.2)***	***0.9 (0.1)***	***0.7 (0.1)***	***0.4 (0.2)***	0.2 (0.2)
Δb	***0.9$_{1}$ (0.6)***	***2.1 (0.6)***	***3.0$_{1}$ (0.5)***	***-0.8 (0.6)***	0.3 (0.3)	0.5 (0.4)	-0.5 (1.0)	-0.7 (0.8)	-0.6 (1.4)	***-0.8 (0.4)***	***-1.5 (1.1)***	-0.3 (1.0)	-0.2$_{12}$ (1.7)	***2.6$_{1}$ (0.8)***	***2.4$_{2}$ (0.7)***	0.7 (0.8)	-0.6 (1.5)	-0.1 (0.7)
ΔE	***1.8$_{1}$ (0.5)***	***2.6 (0.5)***	***3.8$_{1}$ (0.5)***	1.2 (0.4)	1.3 (1.0)	0.9 (0.4)	***1.9 (0.6)***	1.2 (0.6)	1.3 (1.2)	1.2 (0.4)	***2.0 (0.9)***	1.4 (0.7)	***2.0 (1.0)***	***3.2 (0.8)***	***2.7 (0.8)***	1.4 (0.5)	1.6 (1.2)	1.6 (0.5)

Significances ($p<0.05$): *Δ* values and Δ*E*>1 are in bold and italic. Δ*L*, Δ*a*, Δ*b*, and Δ*E* between the curing times and the same curing device of each material are indicated by the same subscript numbers. Δ*E* between the different curing modes of each material are indicated by the bars' endpoints

Differences of Δ*L* and Δ*b* were found between the curing devices (Tables 2 and 3).

Ceram-X Mono was the most color-stable material when water-stored or Suntest-treated, and its LED-light-cured specimens were more color stable than the QTH-light-cured ones (Tables 2 and 3). Ceram-X Mono QTH-light-cured, solely water-stored shifted to more yellow (positive Δ*b*) and less lightness (negative Δ*L*). The 60-s Suntest specimens shifted to yellow, whereas the 10 s cured to more blue (negative Δ*b*). Ceram-X Mono 10-s LED-light-cured shifted to more blue (negative Δ*b*) in both aging tests.

Dyract eXtra was much more color-stable when solely water-stored and did not show very high Δ*E* (Table 2). Immediately after the Suntest, the QTH-light-cured as well as the LED-light-cured specimens behaved similarly for all color values. At the end of the 180-day water storage period, Suntest-treated Dyract eXtra QTH-light-cured samples strongly shifted to more yellow (positive Δ*b*), but LED-light-cured ones did not; they showed strong red shifts (positive Δ*a*; Table 3).

Tetric EvoCeram QTH-light-cured and solely water-stored was less color-stable, showing strong shifts to dark (negative Δ*L*), red (positive Δ*a*), and yellow (positive Δ*b*). The LED-light-cured samples remained rather unchanged (Table 3). After the Suntest and the following 180-day water storage, Tetric EvoCeram severely shifted to yellow (positive Δ*b*), especially when the 10- and 20-s QTH-light-cured specimens were considered (Table 3).

Discussion

The experimental setups followed the literature [10–13, 15–17] and the dental standards [18, 19]. Since the color

Table 3 Means and (standard deviations) after the Suntest followed by 180 days of water storage

	Ceram X Mono						Dyract eXtra						Tetric EvoCeram					
	Halogen			LED			Halogen			LED			Halogen			LED		
	10s	20s	60s	10s	20s	60s	10s	20s	60s	10s	20s	60s	10s	20s	60s	10s	20s	60s
Initial values - Storage: 90 min. dry. room temperature. dark																		
L*	72.2 (0.7)	72.9 (1.1)	74.0 (1.8)	74.5 (1.4)	73.2 (0.8)	73.0 (0.8)	73.2 (0.9)	73.2 (0.7)	73.8 (0.6)	73.1 (0.8)	73.5 (0.9)	73.7 (0.9)	71.4 (0.6)	71.7 (0.6)	71.7 (0.4)	71.9 (0.9)	71.7 (0.6)	71.7 (1.1)
a*	4.2 (0.3)	3.9 (0.3)	3.5 (0.4)	3.1 (0.4)	3.5 (0.2)	3.4 (0.2)	3.8 (0.2)	4.1 (0.3)	4.1 (0.2)	3.9 (0.2)	3.8 (0.2)	3.9 (0.2)	8.3 (0.3)	8.5 (0.2)	8.0 (0.1)	7.6 (0.2)	7.5 (0.3)	7.3 (0.6)
b*	25.5 (0.9)	23.0 (1.3)	21.1 (0.7)	24.6 (1.1)	23.1 (1.0)	22.0 (0.9)	25.4 (0.5)	23.1 (1.2)	20.6 (0.3)	23.1 (0.4)	21.4 (0.5)	19.9 (0.3)	31.2 (0.8)	31.3 (1.0)	31.4 (0.4)	31.1 (0.8)	30.2 (1.2)	29.8 (1.6)
Change of initial values - Storage: Suntest (24 h, water 37 °C)																		
ΔL	0.2$_{12}$ (0.3)	-0.4$_{1}$ (0.4)	-0.6$_{2}$ (0.9)	-0.6$_{12}$ (0.8	***0.4$_{1}$ (0.1)***	0.5$_{2}$ (0.4)	-0.5 (0.5)	-1.1 (0.9)	***-1.2 (0.4)***	***-0.7 (0.4)***	***-0.9 (0.4)***	***-1.0 (0.6)***	***-1.4 (0.3)***	***-1.5 (0.1)***	***-1.0 (0.5)***	***-1.3 (0.2)***	***-1.4 (0.5)***	***-1.4 (0.6)***
Δa	***-0.5$_{12}$ (0.2***	0.1$_{1}$ (0.4)	0.2$_{2}$ (0.4)	0.6 (0.3)	0.0 (0.2)	0.1 (0.3)	***-0.2 (0.1)***	0.2 (0.4)	-0.2 (0.2)	-0.3 (0.2)	***-0.4 (0.1)***	***-0.6 (0.3)***	***-0.3 (0.1)***	***-0.2 (0.1)***	***-0.3 (0.1)***	-0.2 (0.2)	-0.1 (0.3)	-0.2 (0.3)
Δb	***-1.4$_{1}$ (0.9)***	-0.4 (1.7)	***1.5$_{1}$ (0.8)***	***-1.6$_{1}$ (1.0)***	-0.5 (0.4)	0.3$_{1}$ (1.4)	***0.6$_{12}$ (0.2)***	-0.7$_{1}$ (1.5)	***2.4$_{2}$ (0.5)***	-0.3$_{1}$ (0.5)	***1.6$_{1}$ (0.7)***	***3.5$_{1}$ (0.3)***	***1.8 (0.4)***	***2.6 (0.2)***	***1.5 (1.2)***	***1.3$_{1}$ (0.5)***	***2.5 (1.2)***	***3.0$_{1}$ (0.5)***
ΔE	1.6 (0.8)	1.5 (0.9)	***1.9 (0.8)***	***2.1 (0.7)***	0.7 (0.3)	1.4 (0.5)	0.9$_{1}$ (0.3)	***1.9 (0.9)***	***2.7$_{1}$ (0.5)***	1.0$_{1}$ (0.3)	***2.0$_{2}$ (0.5)***	***3.8$_{12}$ (0.3)***	***2.4 (0.4)***	***3.0 (0.2)***	***2.2 (0.4)***	***1.9$_{1}$ (0.4)***	***3.1 (0.8)***	***3.4$_{1}$ (0.6)***
Change of initial values - Storage: 180 d after specimen preparation, water 37 °C. dark																		
ΔL	0.1$_{1}$ (0.1)	***-0.7 (0.5)***	***-1.2$_{1}$ (0.7)***	-0.7 (0.7)	-0.2 (0.9)	0.0 (0.6)	***0.6 (0.1)***	-0.6 (1.0)	-0.7 (0.8)	***-0.8 (0.5)***	***-0.9 (0.3)***	***-0.4 (0.5)***	-0.1 (0.4)	***-0.5 (0.2)***	-0.2 (0.3)	0.1 (0.6)	0.0 (0.8)	1.2 (1.0)
Δa	0.2 (0.2)	***0.3 (0.1)***	0.4 (0.4)	***1.0$_{1}$ (0.2)***	***0.5 (0.1)***	0.4$_{1}$ (0.4)	***0.8$_{1}$ (0.1)***	***0.4 (0.2)***	0.0$_{1}$ (0.2)	***2.0$_{12}$ (0.6)***	***1.4$_{2}$ (0.7)***	***0.5$_{1}$ (0.5)***	***0.4 (0.1)***	***0.4 (0.2)***	0.1 (0.2)	***0.5 (0.2)***	***0.5 (0.3)***	0.1 (0.5)
Δb	***-1.9$_{1}$ (1.0)***	-0.4 (1.5)	***1.2$_{1}$ (0.6)***	***-1.5 (0.8)***	-0.3 (1.0)	0.2 (0.8)	***1.0$_{1}$ (0.1)***	***2.4$_{2}$ (1.2)***	***5.4$_{12}$ (0.4)***	***1.4 (0.5)***	***1.6 (1.6)***	***2.8 (0.4)***	***4.4$_{1}$ (0.4)***	***4.9$_{2}$ (0.4)***	***1.7$_{12}$ (1.3)***	***3.2 (1.2)***	***4.3 (0.9)***	***2.7 (2.0)***
ΔE	***2.0$_{1}$ (0.9)***	1.4 (1.0)	***1.9$_{1}$ (0.7)***	***2.2 (0.6)***	1.1 (0.8)	1.0 (0.5)	***1.4$_{1}$ (0.1)***	***2.6$_{2}$ (1.3)***	***5.5$_{12}$ (0.4)***	***2.7 (0.4)***	***2.8 (0.7)***	***2.9 (0.5)***	***4.4$_{1}$ (0.4)***	***5.0$_{2}$ (0.4)***	***2.0$_{12}$ (1.0)***	***3.3 (1.2)***	***4.4 (0.9)***	***3.3 (1.6)***

Significances ($p<0.05$): *Δ* values and Δ*E*>1 are in bold and italic. Δ*L*, Δ*a*, Δ*b*, and Δ*E* between the curing times and the same curing device of each material are indicated by the same subscript numbers. Δ*E* between the different curing modes of each material are indicated by the bars' endpoints stability depends on the quality of curing, the conversion of the photoinitiator system [10–13, 20, 21], and the materials' formulations, the specimens of different categories of resin-based restorative materials (Table 1) were irradiated with different exposure times. Relevant methods for testing the extent of endogenous discolorations are the Suntest according to EN ISO 7491 [18] and long-term water storage at 37°C to simulate the moist environment of the oral cavity [17, 20, 22]. To get the same endpoint for all test materials, the samples were also stored in water at 37°C for a period of 180 days after the Suntest.

Ceram-X Mono LED-light-cured, solely water-stored samples showed better color stability (lower ΔE) than QTH-light-cured (Table 2), which can be explained by approximately 14% higher radiation doses emitted by the LED light. The increasing yellow shift (positive Δb and therefore negative ΔL) with increasing exposure times of QTH-light-cured Ceram-X Mono samples (Table 2) was highly likely due to the synergist ethyl-4-(*N*,*N*-dimethylamino) benzoate (Table 1). During photopolymerization, initiators or synergists, especially tertiary aromatic amines, form by-products which discolor thermally or under UV light and shift the resin's shade to more red or yellow [12, 23]. The UV/Vis spectrum of ethyl-4-(*N*,*N*-dimethylamino) benzoate shows an absorption at 400 nm and therefore overlaps with the emission spectrum of the quartz–tungsten halogen light. This, in connection with increasing radiation doses at longer exposure times, caused not only an exchange of electrons with camphorquinone but also the formation of shaded by-products. No such behavior was documented for the LED-light-cured, solely water-stored samples because the spectra did not overlap.

QTH-light-cured Suntest and water-stored Ceram-X Mono samples behaved differently, indicating that Δb changed from negative at shorter and to positive at longer exposure times (Table 3). Camphorquinone was completely converted at 10-s irradiation so that the Suntest caused stronger shifts to blue (negative Δb), which was not compensated by the yellow shaded by-products formed by the synergist. Longer exposure times of 60 s totally converted camphorquinone, and the yellowing of the by-products overcompensated the blue shift (Table 3). The same was true for the 10-s LED-light-cured specimens. However, no yellow shift was observed for longer exposure times, which again is predicated on the non-overlapping spectra of LED light and synergist.

Tetric EvoCeram QTH-light-cured and solely water-stored specimens strongly shifted to yellow, but in contrast to Ceram-X Mono, these strong shifts also occurred for the Suntest-treated samples. In addition to the synergist (tertiary aromatic amine, not precisely specified by the manufacturer), Tetric EvoCeram contained not only camphorchinone but also diphenyl-(2,4,6-trimethylbenzoyl)-phosphine oxide as second photoinitiator (Table 1). The absorption maximum of this photoinitiator is at 380 nm, and very likely, it did not completely react or did not even react at all during the irradiation with the LED light, providing an emission spectrum of 430 to 490 nm. While the Suntest was performed, it is assumed that diphenyl-(2,4,6-trimethylbenzoyl)-phosphine oxide decomposed and formed colored by-products. This is in accordance with Uhl et al. [24] who showed that resins containing co-initiators had statistically significant, smaller hardness values at the top and bottom of the samples when LED light was used instead of quartz–tungsten halogen light. They concluded that the LED light did not transform other photoinitiators or synergists that were used in addition to camphorquinone.

Dyract eXtra proved to have good color stability when solely water-stored (Table 2). Although, as Ceram-X Mono, Dyract eXtra contained ethyl-4-(dimethylamino) benzoate as synergist (Table 1), no yellow shift occurred. Probably, there was a higher amount of camphorquinone in Dyract Extra than in Ceram-X Mono so that the blue shift (negative Δb) overcompensated yellowing of the synergist. This explanation was supported by the LED-light-cured samples. On the one hand, due to its emission spectrum, the LED light did not affect the synergist so that the yellowing could not compensate the blue shift. On the other hand, the 10- and 20-s exposure times were not sufficient to adequately transform camphorquinone, which was the case for the 60-s exposure time for which no change of the b^* value was observed.

Since none of the materials significantly shifted to higher lightness (increasing ΔL), all applied exposure times or radiation doses, respectively, were appropriate to nearly completely convert the resin matrix (Tables 2 and 3). Shifts to higher lightness and thus more opaque generally indicate an increased water sorption resulting in a change of the refractive index [25, 26], and it is reported that no such changes take place when the conversion of the matrix is almost complete [11]. However, only a small portion of all materials significantly shifted to red (positive Δa) at the end of both of the aging methods (Tables 2 and 3). This was attributed to the synergists or some of their by-products formed during the initiation process that were thermally or Suntest-attacked and therefore caused the red shifts [12, 23].

The results of the present study showed that the exposure time and radiation dose both influenced internal staining. The emission spectrum of the curing devices and the formulation of the individual material also influenced color stability. LED's emission spectrum was advantageous since no interaction occurred with the synergist so that the formation of shaded by-products could be avoided. The idea of adding a second LED to provide an emission maximum at 400 nm to excite the second photoinitiator, as advertised by a most recently marketed device, does not seem to be beneficial. It might be better to use only photoinitiators within the absorption range of 430 to 490 nm so that no overlapping of synergists can occur. Although the type of monomers (hydrophilic, hydrophobic, aromatic or aliphatic, etc.), the polymeric chain length as a result of reaction kinetics, the types of fillers, or the pigments influenced color stability [10, 12, 13, 16], the photoinitiator system and its interaction with the emission spectrum of the curing light in combination with the applied radiation doses is assumed to dominate color stability [12, 27]. The literature reported differences in color stability when cured with plasma or quartz–halogen light performing different emission spectra [12] or when different amine types were used [27]. However, no direct correlation of radiation dose with color stability was found [16]. The amounts and ratio of photoinitiator and synergist and the combination of photoinitiators and their complex interactions are essential for the polymerization process of resin-based restorative materials and their properties [28–30]. Schneider et al. [28] showed higher amine ratios to improve polymer properties, but also to produce stronger yellow shifts in resin composites.

One limitation of this study is that the exact chemistry of the test materials was not exactly known. Therefore, the effect of different exposure times or of the used curing devices' emission spectra on unknown photoinitiators or synergists and consequently on the color stability might be overestimated. A further limitation was that it was not possible to perform a totally shade-controlled experiment. To eliminate the influence of the shade on the test conditions to a large extent, dentin shade A3 was used for all tested materials, but dentin shade A3.5 was used for Tetric EvoCeram because no A3 was available. However, a rather small differences of the L^*, a^*, and b^* values measured between materials are considered to be acceptable.

Conclusion

When cured with the LED light, similar or even better color stability was achieved with an exposure time of only 10 s than with the quartz–tungsten halogen light and 20-s exposure time. No improvement of color stability was achieved with prolonged irradiation for any of the devices. The null hypothesis was rejected.

Conflict of interest The authors declare that they have no conflict of interest.

References

1. Mobarak E, Elsayad I, Ibrahim M, El-Badrawy W (2009) Effect of LED light-curing on the relative hardness of tooth-colored restorative materials. Oper Dent 34:65–71
2. Fleming GJ, Khan S, Afzal O, Palin WM, Burke FJ (2007) Investigation of polymerisation shrinkage strain, associated cuspal movement and microleakage of MOD cavities restored incrementally with resin-based composite using an LED light curing unit. J Dent 35:97–103
3. Campregher UB, Samuel SM, Fortes CB, Medina AD, Collares FM, Ogliari FA (2007) Effectiveness of second-generation light-emitting diode (LED) light curing units. J Contemp Dent Pract 8:35–42
4. Schneider LF, Consani S, Correr-Sobrinho L, Correr AB, Sinhoreti MA (2006) Halogen and LED light curing of composite: temperature increase and Knoop hardness. Clin Oral Investig 10:66–71
5. Ramp LC, Broome JC, Ramp MH (2006) Hardness and wear resistance of two resin composites cured with equivalent radiant exposure from a low irradiance LED and QTH light-curing units. Am J Dent 19:31–36
6. Martinelli J, Pires-de-Souza Fde C, Casemiro LA, Tirapelli C, Panzer H (2006) Abrasion resistance of composites polymerized by light-emitting diodes (LED) and halogen light-curing units. Braz Dent J 17:29–33
7. Hasler C, Zimmerli B, Lussi A (2006) Curing capability of halogen and LED light curing units in deep class II cavities in extracted human molars. Oper Dent 31:354–363
8. Vandewalle KS, Roberts HW, Andrus JL, Dunn WJ (2005) Effect of light dispersion of LED curing lights on resin composite polymerization. J Esthet Restor Dent 17:244–254 discussion 254–255
9. Correr AB, Sinhoreti MA, Correr Sobrinho L, Tango RN, Schneider LF, Consani S (2005) Effect of the increase of energy density on knoop hardness of dental composites light-cured by conventional QTH, LED and xenon plasma arc. Braz Dent J 16:218–224
10. Janda R, Roulet JF, Latta M, Kaminsky M, Ruttermann S (2006) Effect of exponential polymerization on color stability of resin-based filling materials. Dent Mater 23:696–704
11. Ruttermann S, Servos A, Raab WH, Janda R (2008) In vitro effect of light-emitting diode light polymerization on the color stability of three resin-based restorative materials. Acta Odontol Scand 66:43–49
12. Janda R, Roulet J-F, Latta M, Steffin G, Rüttermann S (2005) Color stability of resin based filling materials after aging when cured with plasma or halogen light. Eur J Oral Sci 113:251–257
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. Eur J Oral Sci 112:280–285
14. Ruyter IE, Oysaed H (1982) Conversion in different depths of ultraviolet and visible light activated composite materials. Acta Odontol Scand 40:179–192
15. Sarafianou A, Iosifidou S, Papadopoulos T, Eliades G (2007) Color stability and degree of cure of direct composite restoratives after accelerated aging. Oper Dent 32:406–411
16. Zamarripa E, Ancona AL, D'Accorso NB, Macchi RL, Abate PF (2008) Effect of energy density on color stability in dental resin composites under accelerated aging. Acta Odontol Latinoam 21:11–15
17. Yazici AR, Celik C, Dayangac B, Ozgunaltay G (2007) The effect of curing units and staining solutions on the color stability of resin composites. Oper Dent 32:616–622
18. EN ISO 7491 (2001) Dental materials—determination of colour stability
19. EN ISO 4049 (2000) Dentistry—polymer-based filling, restorative and luting materials
20. Tanoue N, Koishi Y, Yanagida H, Atsuta M, Shimada K, Matsumura H (2004) Color stability of acrylic resin adhesives with different initiation modes. Dent Mater J 23:368–372
21. Pires-de-Souza Fde C, Garcia Lda F, Hamida HM, Casemiro LA (2007) Color stability of composites subjected to accelerated

aging after curing using either a halogen or a light emitting diode source. Braz Dent J 18:119–123

22. Ertas E, Guler AU, Yucel AC, Koprulu H, Guler E (2006) Color stability of resin composites after immersion in different drinks. Dent Mater J 25:371–376
23. Janda R (1987) Synthetic resins. Ullmann*s encyclopedia of industrial chemistry, vol 8, 5th edn, Chapter 5, Dental materials. VCH, Weinheim, pp 277–284
24. Uhl A, Mills RW, Jandt KD (2003) Photoinitiator dependent composite depth of cure and Knoop hardness with halogen and LED light curing units. Biomaterials 24:1787–1795
25. Ameye C, Lambrechts P, Vanherle G (1981) Conventional and microfilled composite resins. Color stability and marginal adaption. J Prosthet Dent 46:623–630
26. Söderholm KJM (1983) Leaking of fillers in dental composites. J Dent Res 62:126–130
27. Shin DH, Rawls HR (2009) Degree of conversion and color stability of the light curing resin with new photoinitiator systems. Dent Mater 25:1030–1038. http://www.ncbi.nlm.nih.gov/entrez/query.fcgi?cmd=Retrieve&db=PubMed&dopt=Citation&list_uids=19371946
28. Schneider LF, Cavalcante LM, Consani S, Ferracane JL (2009) Effect of co-initiator ratio on the polymer properties of experimental resin composites formulated with camphorquinone and phenyl-propanedione. Dent Mater 25:369–375
29. Ogunyinka A, Palin WM, Shortall AC, Marquis PM (2007) Photoinitiation chemistry affects light transmission and degree of conversion of curing experimental dental resin composites. Dent Mater 23:807–813
30. Park YJ, Chae KH, Rawls HR (1999) Development of a new photoinitiation system for dental light-cure composite resins. Dent Mater 15:120–127
31. Dyract eXtra (2003) Scientific compendium, DeTrey Dentsply GmbH, Constance, Germany
32. Yap AU, Wang X, Wu X, Chung SM (2004) Comparative hardness and modulus of tooth-colored restoratives: a depth-sensing microindentation study. Biomaterials 25:2179–2185
33. Material Safety Data Sheet Tetric EvoCeram (2004) Ivoclar Vivadent Inc., Amherst, NY, USA
34. Scientific Documentation TetricEvoCeram (2005) Ivoclar Vivadent AG, Schaan, Liechtenstein