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ORIGINAL ARTICLE

In vitro effect of light-emitting diode light polymerization on the color stability of three resin-based restorative materials

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Abstract

Objective. To investigate the color stability of resin-based restorative materials when polymerized with light-emitting diode (LED) curing light in the constant or exponential mode. ***Material and methods.*** Eight specimens of Admira (AD), Compoglass F (CO), and Tetric EvoCeram (TE) constantly cured or exponentially cured with a high-powered LED curing light for 10, 20, or 60 s. The CIE-Lab values (L*, a*, b*) were measured prior to and after performing the water storage or color stability test according to EN ISO 7491 (Suntest). ***Results.*** Statistical analysis showed significant changes in the color values after each of the aging processes, as well as between ΔL, Δa, Δb, and ΔE of the materials, which were dependent on curing time, mode, and aging condition ($p<0.05$). CO performed very well during water storage, but AD and TE exceeded the clinically relevant limit $\Delta E = 1$. After the Suntest and 180 d additional water storage, TE showed the highest mean (SD) $\Delta E = 4.4$ (1.1) to 5.4 (1.9). Although AD and CO performed best in the constant mode, they exceeded $\Delta E = 1$. All materials shifted to more red. ***Conclusions.*** The extent of discoloration depended on (a) the curing mode, (b) the curing time, and (c) the aging condition. Not all materials performed clinically acceptably in all tests; TE even showed unacceptable $\Delta E > 3.3$. The optimal curing time was 20 s for both curing modes and all tested materials.

Key Words: *Discoloration, filling, LED, polymerization, resin*

Introduction

Light-emitting diode (LED) curing lights are increasingly being used to polymerize resin-based restorative materials. These very modern curing devices offer advantages such as high power output and very low weight. They can be handled easily, since they are battery operated, and they do not need a power cable. LED curing lights can be operated in the constant as well as the exponential (soft start) mode. Although the first generation devices did not perform well [1,2], the latest generation is reported to work optimally [3–9]. These investigations focused only on the physical properties and did not consider the color stability of LED light polymerized resin-based restorative materials. However, color stability is essential in tooth-colored restorative materials.

Color stability of resin-based restorative materials is influenced by the photoinitiator system, the resin matrix, the light-curing device used for polymerization, and irradiation times [10–15]. Although used in very small amounts, the most commonly used photoinitiator camphorquinone significantly influences the color of the material [10]. Other very important components of photoinitiator systems are tertiary aromatic or aliphatic amines, which act as so-called synergists or accelerators [10] and can form by-products during photoreaction that tend to cause yellow to red-brown discolorations under the influence of light or heat [16]. The influence of the resin matrix on color stability is also known. If the matrix is more hydrophilic, an increased water sorption occurs and the shade shifts to white and opaque [15], but if it is very hydrophobic the water sorption is less and only a small impact on the color is seen [12–15,17]. Also the type of filler might influence the color [15,17]. However, it is reported in the literature [20] that color stability of resin-based restorative materials depends on the curing mode (exponential or constant). To obtain acceptable color stability, 60 s exponential curing rather than 40 s constant curing is

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required when polymerized with halogen curing devices. Therefore, it is important to know whether high-power LED curing lights also require prolonged exponential curing time for good color stability to be achieved.

The aim of this investigation was to determine the effect of LED light polymerization in constant or exponential mode on the color stability of contemporary resin-based restorative materials as a function of curing times and aging conditions. The research hypothesis was that there is no influence of (a) curing mode, (b) curing time, or (c) aging condition on the color stability of contemporary resin-based restorative materials.

Material and methods

Three types of contemporary light-curing resin-based restorative material were chosen (Table I) to investigate whether the composition influenced the results. To largely eliminate the influence of shade on the test conditions, dentin shade A3 was used for two tested materials. Only dentin shade A3.5 was available for Tetric EvoCeram (TE). The LED curing light bluephase (Ivoclar Vivadent AG, Schaan, Liechtenstein) was used for polymerization. According to the manufacturer, bluephase emits light between 430 and 490 nm and provides a maximum power output of 1100 ± 110 mW cm^{-2} when the 8 mm diameter light guide is used. Using the exponential mode, the power output increases to 650 mW cm^{-2} within 5 s and then to 1100 mW cm^{-2}.

The 10 mm diameter light guide was used in the study. A maximum power output of 900 ± 10 mW cm^{-2} was measured with the Curing Light Meter (Benlioglu Dental Inc. Ankara, Turkey) when the light guide was put directly on the sensor. Light intensity was checked each time after each series of eight specimens was cured. From each test material, 6 groups of 16 specimens each (thickness: 1.0 ± 0.1 mm, diameter: 10 ± 0.1 mm), 288 specimens in total (Figure 1), were prepared at 22.0–22.5°C room temperature and a relative humidity of 50%. Prior to irradiation, both sides of the specimens were covered with a 0.05 mm transparent polyester film to avoid an inhibition layer. The specimens were polymerized in one step and from one side only by fixing the light guide (diameter: 10 mm) at a distance exactly 5 mm from the surface to ensure that they were uniformly irradiated. To evaluate whether the decrease in light intensity was acceptable, it was measured from this distance and a reduction of only 12% was found (resulting power output: 790 ± 11 mW cm^{-2}).

Each group was divided into two subgroups of eight specimens each, and the specimens of each material group were randomly allocated to the subgroups. Group 1 was constantly irradiated for 10 s, group 2 for 20 s, and group 3 for 60 s. Group 4 was exponentially irradiated for 10 s, group 5 for 20 s, and group 6 for 60 s. From each group, subgroup 1 was put in water storage at 37°C and for subgroup 2 the Suntest was performed according to EN ISO 7491 [18] using the Suntest CPS+ device (Atlas Material Testing Technology GmbH, Linsengericht, Germany) followed by additional water storage at 37°C.

The $L^\star$, $a^\star$, and $b^\star$ values ($L^\star$ = lightness, $+a^\star$ = red, $-a^\star$ = green, $+b^\star$ = yellow, $-b^\star$ = blue) were measured prior to and after aging, and the total color change ΔE ($\Delta E = \sqrt{(\Delta L^2 + \Delta a^2 + \Delta b^2)}$), as well as ΔL, Δa, and Δb, was calculated. Color measurements of all specimens were made the first time after 90 min of dry and dark storage at room temperature to obtain the color values at the earliest possible time, since color changes may occur even after 1 d of dry and dark storage [19,20]. For the water storage

Table I. Test materials.

Material	Composition	Manufacturer
Admira A3 #540267 (Ormocer)	• Resin matrix: aromatic and aliphatic dimethacrylates, methacrylate-functionalized polysiloxane • Inorganic filler: Ba-Al-glass, pyrogenic SiO_2, filler load: 78 mass % • Photoinitiator: camphorquinone • Synergist: NI	Voco GmbH, Cuxhaven, Germany
Compoglass F A3 #H09924 (Compomer)	• Resin matrix: UDMA, TEGDMA, cycloaliphatic dicarboxylic acid dimethacrylate • Inorganic filler: Ba-Al-fluorosilicate glass, pyrogenic SiO_2, ZrO_2, YF_3, filler load: 77 mass % • Photoinitiator: camphorquinone • Synergist: NI	Ivoclar Vivadent AG, Schaan, Liechtenstein
Tetric EvoCeram A3.5 #H03360 (Hybrid)	• Resin matrix: UDMA, Bis-GMA, ethoxylated Bis-EMA • Inorganic filler: Ba-glass, Al_2O_3, Yb_3, pyrogenic SiO_2, filler load: 48.5 mass % • Pre-polymer filled with pyrogenic SiO_2, filler load: 34.0 mass % • Photoinitiator: camphorquinone, diphenyl (2,4,6-trimethybenzoyl)-phosphine oxide • Synergist: tertiary amine	Ivoclar Vivadent AG

Bis-GMA = Bisphenol-A-dimethacrylate, UDMA = urethane dimethacrylate, TEGDMA = triethyleneglycol dimethacrylate, NI = no information.
Compositions were taken from the literature: Admira [23,24], Compoglass F [25–27], Tetric EvoCeram [28].

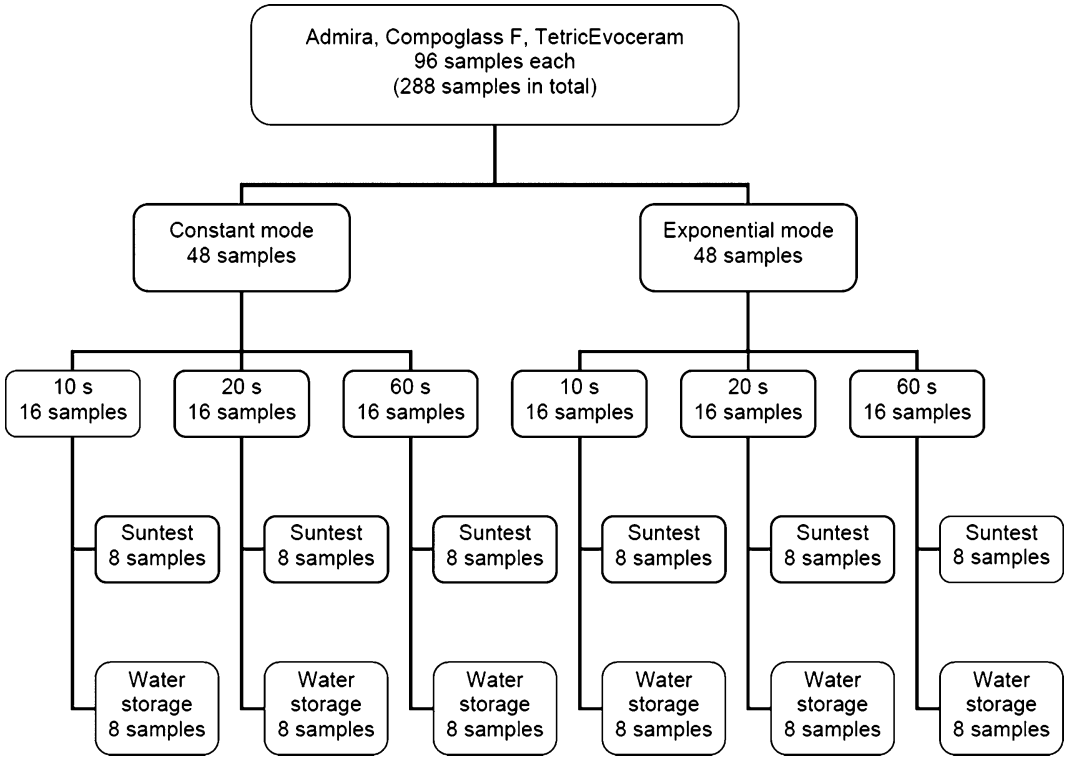

Figure 1. Experimental setup.

groups, the next color measurement was made after 180 d. For the Suntest groups, further measurements were made directly after the Suntest and after 180 d water storage at 37°C in the dark [10,19,20]. All wet specimens were blot-dried prior to color measurement. After termination of the Suntest, the specimens were blot-dried and measured again 1 h later. Color was measured from the irradiated sides of the specimens using the 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 v. 12.01 (SPSS, Chicago, Ill., USA). Means and standard deviations were calculated. Normal distribution was confirmed by the Kolmogorov–Smirnov test. Generalized linear model (GLM) and repeated measures analysis of variance (ANOVA) were calculated to evaluate significant differences for each material's curing mode and time on L*, a*, and b* prior to and after aging. Statistical analysis was done with the repeated measures ANOVA, since the measurements for each of these values were made on the same sample. Four-way ANOVA was calculated to investigate the influence of the independent variables material, curing time, curing mode, and aging on ΔL, Δa, Δb, and ΔE. Multiple comparisons of ΔL, Δa, Δb, and ΔE between the materials' curing times and curing modes were done with the multivariate ANOVA followed by a Bonferroni post hoc test. Significant deviations of each ΔE from the limit values 1 and 3.3 were calculated with the lowest significant difference ANOVA. Statistical significance was considered as $p<0.05$ for all tests.

Results

Color measurements are given in Tables II and III. Changes in the L*, a*, and b* values below 1 are presented in the tables. These are not discussed in the text since they are considered not to be of clinical relevance [19–21]. The GLM and the repeated measures ANOVA revealed significant changes in the color values for each material's curing time and curing mode prior to and after aging. Four-way ANOVA and Bonferroni's post hoc test revealed significant differences ($p<0.05$) between the ΔL, Δa, Δb, and ΔE values of the materials, which were dependent on the curing mode, curing time, and aging condition. The type of material significantly influenced ΔL ($p<0.001$), Δa ($p<0.002$), and ΔE ($p<0.007$). The extent of Δb was independent of the material. Significant differences were also found between ΔL ($p<0.004$), Δa ($p<0.001$), Δb ($p<0.001$), and ΔE ($p<0.049$) of the materials in dependence on curing time. According to the aging conditions, the materials differ significantly from each other referring to ΔL ($p<0.001$), Δa ($p<0.001$), Δb ($p<0.001$), and ΔE

Table II. Means and (standard deviations) after 180 d water storage.

	Admira						Compoglass F						TetricEvoCeram					
	Constant			Exponential			Constant			Exponential			Constant			Exponential		
	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*	76.9 (1.4)	77.3 (1.0)	76.5 (1.2)	78.5 (1.7)	79.1 (1.7)	78.4 (1.3)	78.3 (0.9)	79.3 (1.5)	78.7 (1.0)	78.8 (1.0)	79.9 (0.8)	80.1 (1.2)	74.7 (0.7)	74.9 (0.7)	73.8 (0.7)	75.2 (0.7)	75.3 (0.9)	74.6 (0.6)
a*	2.3 (0.5)	2.9 (0.2)	2.7 (0.3)	2.1 (0.2)	2.6 (0.4)	2.7 (0.4)	3.0 (0.6)	2.7 (0.7)	2.8 (0.3)	3.0 (0.3)	2.8 (0.3)	2.6 (0.8)	6.4 (0.6)	7.0 (0.5)	6.4 (0.3)	6.7 (0.5)	6.8 (0.3)	6.7 (0.3)
b*	22.6 (1.7)	22.5 (1.7)	20.6 (0.6)	23.7 (0.8)	21.4 (1.4)	19.4 (1.1)	33.2 (1.0)	31.7 (1.4)	30.7 (1.3)	33.1 (0.8)	32.3 (0.7)	30.5 (1.6)	29.5 (0.5)	29.4 (0.7)	27.6 (1.0)	30.5 (0.7)	30.0 (0.6)	28.2 (0.7)
Change of initial values – Storage: 180 d, water 37°C, dark																		
ΔL	1.0 (1.3)	0.8 (0.9)	0.6 (0.7)	−1.3 (1.4)	***−2.3 (1.5)***	***−2.2 (1.4)***	0.8 (0.8)	1.0 (1.5)	0.6 (0.8)	***1.3 (0.7)***	0.1 (0.6)	0.3 (1.1)	−1.3 (1.0)	***−1.7 (0.7)***	***−0.7 (0.3)***	***−2.0 (2.0)***	***−1.5 (0.5)***	***−1.7 (0.5)***
Δa	***0.3 (0.1)***	0.3 (0.2)	***0.3 (0.2)***	***0.8 (0.2)***	***0.5 (0.4)***	0.5 (0.4)	***0.9 (0.4)***	0.6 (0.6)	0.6 (0.4)	***0.3 (0.2)***	***0.7 (0.3)***	0.6 (0.5)	***1.4 (0.9)***	***0.9 (0.5)***	***1.2 (0.2)***	***1.1 (0.6)***	***1.2 (0.4)***	***1.1 (0.3)***
Δb	−1.7 (2.0)	−0.8 (1.2)	0.5 (1.2)	0.0 (2.3)	0.3 (1.0)	1.0 (1.1)	0.0 (1.1)	−0.1 (1.4)	0.7 (0.7)	−0.7 (0.8)	0.5 (0.5)	0.6 (1.1)	0.0 (1.4)	0.4 (0.7)	***1.6 (0.5)***	***−0.7 (0.4)***	***1.2 (0.7)***	***1.3 (0.5)***
ΔE	***2.2 (2.2)***	1.4 (1.3)	1.4 (0.8)	***2.8 (1.3)***	***2.8 (1.1)***	***3.0 (0.8)***	1.8 (0.5)	2.0 (1.3)	1.5 (0.6)	1.8 (0.3)	1.2 (0.3)	1.8 (0.3)	***2.7 (0.7)***	***2.2 (0.4)***	***2.2 (0.4)***	***2.9 (2.1)***	***2.4 (0.5)***	***2.5 (0.2)***

Significant Δ-values and ΔE significantly >1 are in bold and italic ($p<0.05$).

($p<0.001$). Significant differences related to the curing mode were only found between Δb ($p<0.004$) and ΔE values ($p<0.002$).

Since $\Delta E \geq 1$ is considered to be of clinical relevance and $\Delta E \geq 3.3$ to be unacceptable [21], significant differences ($p<0.05$) between each of the ΔE values and the limits of $\Delta E = 1$ or $\Delta E = 3.3$, respectively, were calculated. Admira (AD) constantly cured for 10 s, and all exponentially cured specimens, as well as all TE specimens, significantly (significances between $p>0.001$ and $p<0.04$) exceeded $\Delta E = 1$ after 180 d dark storage in water at 37°C (Table II). None of the Compoglass F (CO) specimens showed ΔE significantly above 1. Immediately after the Suntest (Table III), all materials, except CO exponentially cured for 60 s and TE exponentially cured for 60 s, exceeded $\Delta E = 1$ (significances between $p<0.001$ and $p<0.042$). After the subsequent 180 d period in water at 37°C, all materials significantly exceeded $\Delta E = 1$ (significances between $p<0.001$ and $p<0.005$), but TE constantly cured for 60 s ($p<0.032$) and exponentially cured for 10 s ($p<0.001$) even exceeded $\Delta E = 3.3$ (Table III).

The total color change ΔE measured immediately after the Suntest increased significantly after 180 d water storage at 37°C for 20 s ($p<0.001$) and 60 s ($p<0.016$) constantly cured and 10 s ($p<0.021$) and 60 s ($p<0.001$) exponentially cured TE and 10 s ($p<0.029$) and 20 s ($p<0.014$) exponentially cured CO specimens.

The L* value of AD after water storage at 37°C (Table II) was significantly lower than the starting L* (dark shift) for the 20 s and 60 s exponentially cured specimens, and the a* value increased (red shift) for all curing modes and times except for the 20 s constantly cured and the 60 s exponentially cured groups. All constantly cured and exponentially cured TE specimens showed significantly lower L* values (dark shift) and higher a* values (red shift) after water storage. Significantly, higher b* values (yellow discoloration) compared with the start were found for the 60 s constantly cured and the 20 s and 60 s exponentially cured specimens (Table II).

Immediately after the Suntest (Table III), most of the materials shifted to dark and to more red (significant decrease of L* and increase of a*). The largest positive Δa resulted when AD and TE were exponentially cured for 10 s. AD constantly cured or exponentially cured for 60 s showed yellowing (significant positive Δ of b*). CO, when constantly cured for 10 s and TE, when exponentially cured for 10 s, bleached (significant negative Δ of b*) (Table III).After the Suntest (Table III) and subsequent 180 d additional storage at 37°C in water, the AD specimens that had been exponentially cured for 20 s were significantly darker than the initial values. All Δb values remained unchanged when compared with the Suntest results. All exponentially cured CO

Table III. Means and (standard deviations) after Suntest followed by 180 d water storage.

	Admira						Compoglass F						TetricEvoCeram					
	Constant			Exponential			Constant			Exponential			Constant			Exponential		
	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*	78.4 (1.1)	77.9 (1.8)	78.2 (1.5)	77.9 (1.2)	78.7 (1.2)	77.5 (1.1)	78.5 (0.6)	78.9 (1.1)	79.1 (1.0)	78.7 (0.7)	78.2 (0.9)	78.0 (0.8)	74.4 (1.3)	73.7 (0.8)	74.8 (0.9)	71.0 (0.5)	73.3 (1.2)	73.1 (0.9)
a*	2.3 (0.4)	2.5 (0.4)	2.8 (0.5)	2.3 (0.2)	2.6 (0.3)	2.5 (0.2)	3.2 (0.3)	2.5 (0.4)	2.8 (0.5)	3.3 (0.3)	3.1 (0.2)	2.9 (0.3)	6.8 (0.6)	5.8 (0.7)	6.4 (0.5)	5.1 (0.5)	6.1 (0.7)	6.2 (0.5)
b*	24.2 (1.3)	21.6 (1.4)	21.3 (0.9)	25.4 (0.5)	22.6 (0.9)	19.7 (0.6)	33.5 (0.6)	31.6 (1.5)	31.3 (1.1)	33.4 (0.7)	32.1 (1.1)	30.7 (0.5)	29.3 (1.3)	27.9 (0.8)	28.0 (0.8)	25.5 (0.7)	27.6 (1.2)	26.9 (0.7)
Change of initial values – Storage: Suntest (24 h, water 37°C)																		
ΔL	***−1.6 (1.0)***	−1.1 (1.4)	***−2.2 (1.2)***	***−2.2 (1.3)***	***−3.3 (1.9)***	−1.5 (1.2)	0.2 (0.6)	−1.4 (1.1)	***−1.8 (1.1)***	−0.4 (0.5)	−0.2 (0.7)	0.6 (0.6)	−1.4 (1.4)	−0.8 (0.7)	***−1.0 (0.7)***	***1.9_{12} (0.7)***	-0.7_{1} (1.3)	-0.7_{2} (0.8)
Δa	***1.4 (0.6)***	***0.7 (0.5)***	0.7 (0.8)	***2.4 (0.9)***	0.8 (0.6)	***0.7 (0.4)***	***0.6 (0.2)***	0.5 (0.4)	***0.8 (0.5)***	−0.7 (0.6)	***0.7 (0.1)***	***0.9 (0.2)***	1.2 (0.9)	0.4 (0.7)	0.2 (1.1)	***2.2_{12} (0.6)***	0.5_{1} (0.5)	0.1_{2} (0.5)
Δb	−0.8 (1.4)	0.9 (1.2)	***1.8 (1.1)***	-1.1_{1} (0.9)	-0.4_{2} (1.2)	***2.4_{12} (1.2)***	***-3.6_{12} (1.3)***	1.2_{1} (1.3)	1.8_{2} (1.4)	−2.0 (1.8)	−0.3 (1.7)	−1.9 (1.4)	−0.5 (1.7)	0.2 (1.9)	−0.3 (2.0)	***2.5 (1.7)***	−1.2 (1.0)	−0.5 (0.9)
ΔE	***2.9 (0.6)***	***2.3 (1.1)***	***3.4 (0.9)***	***3.8 (0.9)***	***3.8 (1.6)***	***3.1 (1.2)***	***3.7 (1.3)***	***2.4 (1.1)***	***3.1 (1.0)***	***2.5 (1.6)***	1.7 (1.0)	***2.3 (1.3)***	***2.9 (0.8)***	***2.2 (0.6)***	***2.4 (1.0)***	***3.9 (1.7)***	***2.1 (0.7)***	1.5 (0.5)
Change of initial values – Storage: 180 d after specimen preparation, water 37°C, dark																		
ΔL	−1.3 (1.3)	−0.6 (1.4)	−1.2 (1.4)	−1.6 (1.3)	***−2.6 (1.3)***	−0.8 (0.6)	***1.2 (0.3)***	0.3 (0.9)	0.0 (1.3)	***1.3 (0.6)***	***1.8 (0.5)***	***2.1 (0.5)***	***−1.6 (0.9)***	***−1.7 (0.4)***	***−2.5 (0.8)***	1.6_{12} (2.0)	-0.9_{1} (1.9)	-1.1_{2} (0.8)
Δa	***1.3 (0.4)***	***1.2 (0.4)***	***0.8 (0.4)***	***1.5 (0.4)***	***1.1 (0.3)***	***1.1 (0.2)***	***1.0 (0.2)***	***1.3 (0.4)***	***1.1 (0.3)***	***1.0 (0.6)***	***1.1 (0.2)***	***1.1 (0.1)***	***1.4 (0.4)***	***1.7 (0.4)***	***1.6 (0.3)***	***2.7_{12} (0.6)***	***1.6_{1} (0.6)***	***1.5_{2} (0.4)***
Δb	−0.9 (1.0)	1.0 (1.2)	***1.3 (0.9)***	***-2.3_{1} (0.6)***	0.2_{1} (1.1)	***2.4_{1} (0.8)***	***-2.0_{12} (1.1)***	1.6_{1} (1.5)	***1.1_{2} (0.9)***	***−3.3 (1.2)***	−1.1 (2.2)	−1.6 (1.6)	0.4_{1} (1.5)	***3.2_{1} (1.4)***	2.9 (1.5)	2.5 (3.6)	0.6 (1.4)	***2.1 (1.0)***
ΔE	***2.5 (0.9)***	***2.4 (0.6)***	***2.6 (0.4)***	***3.5 (0.8)***	***3.1 (1.1)***	***2.9 (0.8)***	***2.6 (0.8)***	***2.5 (1.0)***	***1.5 (0.4)***	***3.8 (1.1)***	***3.1 (1.1)***	***3.1 (1.0)***	***2.7 (0.5)***	***4.1 (1.3)***	***4.4 (1.1)***	***5.4_{12} (1.9)***	***3.0_{1} (0.9)***	***3.0_{2} (0.8)***

Significances ($p<0.05$): (a) Δ-values and ΔE significantly >1 are bold and italic, (b) ΔL, Δa, Δb, ΔE between the curing times of the same curing mode of the same material are indicated by same subscript numbers, (c) ΔE between the different curing modes of the same material are indicated by lines with black dots.

specimens as well as the 20 s constantly cured ones shifted to more white (significant positive Δ of L*) when compared with the initial values (Table III). The 10 s constantly or exponentially cured specimens bleached (significant negative Δ of b*), but the 60 s constantly cured ones shifted to more yellow (significant positive Δ of b*). All constantly cured TE specimens shifted to dark (significant negative Δ of L*) when compared with the initial values. TE specimens that had been constantly or exponentially cured for 20 s or 60 s showed higher positive Δa when compared with the Suntest values. Yellow shifts were observed for the 20 s constant and the 60 s exponential curing times (Table III). All test materials shifted to more red (significant positive Δ of a*) irrespective of the curing time or curing mode (Table III).

Discussion

Although the color stability of resin-based restorative materials has been investigated when cured in the constant or exponential curing mode [10,19,20], no literature was found for the high-power LED curing lights. Therefore, the present investigation examined the influence of the different curing modes of these curing lights on the color stability of various materials. Test methods, specimen size, and irradiation modes followed well-proven experimental setups [10,19,20]. Since color stability depends on the quality of curing and on the conversion of the photoinitiator system, the specimens were irradiated for 10, 20, or 60 s in the constant or exponential curing mode. To get the same endpoint for all test materials and to investigate whether further color changes occurred, the specimens were also stored in water at 37°C for a period of 180 d after the Suntest. 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. ΔE significantly above 1 was considered to be visible with the naked eye and $\Delta E \geq 3.3$ as clinically unacceptable [10,19–21].

None of the CO specimens except the 10 s constantly cured and all exponentially cured AD specimens and all the TE specimens exceeded $\Delta E = 1$ after 180 d water storage (Table II). This clearly indicated the crucial influence of the materials' composition on color stability, which has been reported in the literature [20]. However, the mild aging in water at 37°C did not result in a clear differentiation between constantly or exponentially cured materials when aged differently.

After the Suntest (Table III), all AD, CO (except for 20 s exponentially cured) and TE (except for 60 s exponentially cured) specimens showed ΔE significantly above 1. No further increase of ΔE for AD during the following 180 d water storage indicated the complete cure of this material for all curing times and both of the curing modes. Constant (10 s, 20 s, constant, and 20 s exponential, respectively) or increasing Δb (60 s constant and exponential) indicated that camphorquinone reacted completely due to the intense LED light and therefore no bleaching could compensate the yellowing effect caused by the very strong Suntest light [10,19,20]. ΔE of CO exponentially cured and TE specimens further increased (Table III), proving the influence of water on color stability. CO constantly cured seemed to be superior to the exponentially cured specimen. This assumption is supported by significant shifts to white and thus more opaque that indicated an increased water sorption resulting in a change of the refractive index [17,22]. The water sorption was certainly not caused just by the very hydrophilic matrix containing cycloaliphatic dicarboxylic acid dimethacrylate (Table I), but also by an incomplete conversion of the matrix since the constantly cured specimens (20 s and 60 s) did not show these shifts. The strong bleaching of CO also showed that the photoinitiator camphorquinone did not fully react. TE was the most color-unstable material in this test with the highest ΔE values after the additional 180 d storage in water that were predominantly due to strong red and yellow discolorations. TE did not bleach at all. TE constantly cured for 60 s and exponentially cured for 10 s significantly exceeded the limit of $\Delta E = 3.3$. These unacceptable ΔE values, which were mainly due to strong shifts to dark and red for the 60 s constantly cured and to white and red for the 10 s exponentially cured specimens, are assumed to be caused by not completely reacted photoinitiator components. This is considered further below.

As reported, curing with the tungsten halogen light always resulted in significant bleaching effects following the Suntest when constantly cured for 20 s only [10,19]. This means that the camphorquinone did not totally react during the polymerizing process. The results of the present study showed significant bleaching only for the 10 s constantly or exponentially cured CO as well as the 10 s exponentially cured AD specimens after the Suntest followed by 180 d water storage. This indicated that the LED curing light emitted not only very intense light (approx. 1000 mW cm^{-2}), but also had the optimal emission spectrum (430 to 490 nm) for totally transforming camphorquinone to colorless products at irradiation of 20 s or longer. Uhl et al. [5] showed that composites containing co-initiators had statistically significant, smaller hardness values at the top and bottom of the specimens when LED light was used instead of halogen light. They concluded that the LED light did not transform other photoinitiators or synergists that were used in addition to camphorquinone. Under the limitations of the present study, this conclusion can be confirmed, since significant red

shifts of all investigated materials were observed to an extent that has not been reported in the literature [10,19]. Some materials shifted to more yellow, too. Such color changes are known to be caused by yellow-red by-products of not completely reacted photoinitiators or synergists such as tertiary aromatic amines [16,19]. Very strong red and yellow shifts, even resulting in $\Delta E > 3.3$, occurred for TE, which contains a phosphine oxide photoinitiator in addition to camphorquinone. The absorption maximum of this initiator is at 380 nm, so it is suspected that it did not completely react, or even did not react at all, during the irradiation with the LED curing light (emission spectrum 430 to 490 nm).

The effect of the LED light not to transform photoinitiators or synergists used in addition to camphorquinone might be overestimated, since the exact composition of each of the test materials is unknown. To be certain, the chemistry and absorption spectra of these components must be known. The resin matrix as well as the type of filler might also influence color stability [19,20]. Another limitation of this study is that only internal discolorations were considered. The influence of external stains such as coffee, tea, cigarettes, drugs, etc., was not investigated. However, the results give some evidence about the material-inherent properties.

Conclusions

When cured with LED light, the color stability of the investigated resin-based restorative materials depended on various factors, namely the curing mode, the curing time and the aging condition. Not all materials performed clinically acceptably in all tests, some even showed unacceptable $\Delta E > 3.3$. The best results were obtained with a curing period of 20 s for both curing modes. The color stability of the materials depended on (a) curing mode, (b) curing time, and (c) aging condition. The research hypothesis was therefore rejected.

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