©*Operative Dentistry, 2007,* **32-4**, 406-411

Color Stability and Degree of Cure of Direct Composite Restoratives After Accelerated Aging

A Sarafianou • S Iosifidou
T Papadopoulos • G Eliades

Clinical Relevance

Accelerated hydrothermal- and photo-aging of direct light-cured composite restorative materials induced visually perceptible but clinically acceptable total color changes, along with a reduction in the amount of remaining C=C bonds.

SUMMARY

Purpose: This study evaluated the color changes and amount of remaining C=C bonds (%RDB) in three dental composites after hydrothermal- and photoaging. Methods and Materials: The materials tested were Estelite Σ, Filtek Supreme and Tetric Ceram. Specimens were fabricated from each material and subjected to L* a* b* colorimetry and FTIR spectroscopy before and after aging. Statistical evaluation of the ΔL,* Δa,* Δb,* ΔE and %ΔRDB data was performed by one-way ANOVA and Tukey's test. The %RDB data before and after aging were statistically analyzed using two-way ANOVA and Student-Newman-Keuls test. In all cases an $\alpha=0.05$ significance level was used. Results: No statistically significant differences were found in ΔL*, Δa*, ΔE and %ΔRDB among the materials tested. Tetric Ceram demonstrated a significant difference in Δb*. All the materials showed visually perceptible (ΔE>1) but clinically acceptable values (ΔE<3.3). Within each material group, statistically significant differences in %RDB were noticed before and after aging ($p<0.05$). Filtek Supreme presented the lowest %RDB before aging, with Tetric Ceram presenting the lowest %RDB after aging ($p<0.05$). The %ΔRDB mean values were statistically significantly different among all the groups tested. No correlation was found between ΔE and %ΔRDB.

INTRODUCTION

Currently available composites provide satisfactory strength and high esthetic appearance. However, despite

---

Aspasia Sarafianou, DDS, PhD, Department of Prosthodontics, School of Dentistry, National and Kapodistrian University of Athens, Athens, Greece

Soultana Iosifidou, BS, Physics, Department of Biomaterials, School of Dentistry, National and Kapodistrian University of Athens, Athens, Greece

*Triantafillos Papadopoulos, associate professor, Department of Biomaterials, School of Dentistry, National and Kapodistrian University of Athens, Athens, Greece

George Eliades, professor, Department of Biomaterials, School of Dentistry, National and Kapodistrian University of Athens, Athens, Greece

*Reprint request: 2 Thivon Str, 11527, Athens, Greece; e-mail: trpapad@dent.uoa.gr

DOI: 10.2341/06-127

recent improvements, color stability of light-cured composites after long-term intraoral exposure remains a concern.[1] Various studies have shown that the color stability of composites can be influenced by several extrinsic factors, such as intensity and duration of the polymerization,[2-3] exposure to environmental factors, including ambient and UV radiation,[4] heat, water[5] or food colorants.[6-8] Moreover, color stability is also affected by intrinsic factors, such as the composition of the resin matrix, filler loading and particle size distribution,[9] type of photoinitiator[10] and percentage of remaining C=C bonds (%RDB).[11] The latter is considered a fundamental parameter influencing a variety of mechanical, chemical and biological properties.[12-14]

To simulate testing of the long-term intraoral color stability of composites, several *in vitro* methods have been developed, including storage in water and in dark and dry conditions,[2] exposure to visible and UV radiation or to several food staining solutions.[15-16]

This study evaluated the color stability and amount of %RDB of three direct composite restorative materials after artificial aging.

The study hypothesis was that the color parameters of the materials tested would remain within a clinically acceptable level after aging, whereas, significant differences exist in %RDB.

Table 1: *Composition of the Materials Tested*

Composites	Composition	Manufacturer
Estelite Σ	Resin: BisGMA, TEGDMA ZrO_2/SiO_2 Fillers: 82% wt, 71% v 0.2 μm mean size	Tokuyama Dental Corp, Tokyo, Japan
Filtek Supreme	Resin: BisGMA, BisPMA DUDMA, TEGDMA Fillers: SiO_2 nanofiller (20 nm) ZrO_2/SiO_2 nanoclusters (0.6-1.4 μm size) 78.5% wt, 59% v	3M ESPE St Paul, MN, US
Tetric Ceram	Resin: BisGMA, UDMA, TEGDMA Fillers: Silanated $BaAlFSiO_4$ Ba-glass, SiO_2, YF_3 79% wt, 60% v 0.7 μm mean size	Ivoclar Vivadent, Schaan, Lichtenstein

BisGMA: Bisphenol-A-diglycidyl methacrylate, BisPMA: Bisphenol-A-polyehylene glycol diether dimethascylate, DUDMA: diurethane dimethacrylate, TEGDMA: triethylene glycol dimethacrylate, UDMA: urethane dimethacrylate

Table 2: *Results of the Color Parameters*

Composites	ΔL*	Δa*	Δb*	ΔE
Estelite Σ	0.86 ± 0.39^a	-0.5 ± 0.81^b	-2.68 ± 0.47^c	2.96 ± 0.56^f
Tetric Ceram	1.22 ± 1.82^a	-1.6 ± 1.53^b	0.42 ± 1.01^d	2.78 ± 1.51^f
Filtek Supreme	0 ± 1.18^a	0 ± 0.68^b	1.06 ± 1.20^c	1.80 ± 1.42^f

Same superscripts indicate mean values with no statistically significant differences (p<0.05) among the materials tested.

METHODS AND MATERIALS

Two light-cured microhybrid restorative resin composites (Estelite Σ and Tetric Ceram) and one nanofilled composite (Filtek Supreme) were tested. All the materials were of the A2 shade (Table 1).

Specimen Preparation

Metal rings (1.2 mm in height and 8.5 mm in diameter) were filled with each composite paste, pressed between two microscopic glass slides covered with transparent polystyrene matrix strips to remove excess material and light-cured for 40 seconds under standard conditions (850 mW/cm^2, 500-400 nm) using a halogen curing unit (Trilight, 3M ESPE, Seefeld, Germany). Five specimens were prepared from each material.

Aging

The specimens were subjected to hydrothermal-cycling (2000X, 5°/55°C, 3 c/minute), then photoaged in a weathering apparatus (Suntest CPS+, Atlas, Chicago, IL, USA) operated under the following conditions: 800-300 nm wavelength, 765 W/m^2 irradiance, 66 MJ/m^2 daily radiant exposure, 37°C chamber temperature and 98 hour exposure time.

Colorimetry

The color of the specimens before and after aging was measured with a portable colorimeter (Dr Lange Microcolor Data Station, Braive Instruments, Liege, Belgium). Specimen orientation against the colorimeter head was standardized by a custom-made specimen holder. The measurements were performed according to the CIE L*a*b* system and the mean L*, a* and b* values for each material calculated. The total color change (ΔE) obtained was calculated for each specimen using the equation: $\Delta E = [(\Delta L^*)^2 + (\Delta a^*)^2 + (\Delta b^*)^2]^{1/2}$, where ΔL*, Δa* and Δb* are differences in the respective values before and after aging. Color changes were considered visually perceptible when $\Delta E > 1$ and clinically acceptable when $\Delta E < 3.3$.[15-17]

Degree of Cure

The degree of cure of the composite specimens before and after aging was evaluated by FTIR spectroscopy, employing a micro-MIR accessory (Perkin Elmer Corp, Norwalk, CT, USA) attached to an FTIR spectrometer (Spectrum GX, Perkin Elmer Corp). Spectra were acquired under the following conditions: 4000-400 cm^{-1} range, 4 cm^{-1} resolution, 60° para-edge KRS-5 mini-crystal (10x5x1 mm) of seven internal reflections, 50 scans coaddition at 23±1°C and ~1 µm sampling depth at 1000 cm^{-1}. Three specimens were analyzed per composite. Spectra of the unset pastes were used as a reference. Quantitative measurements of the percentage amount of remaining C=C bonds (%RDB) were performed based on the two-frequency technique. The aliphatic C=C vibrations (1638 cm^{-1}) were used as the analytical frequency; whereas, the aromatic C…C vibrations (1605 cm^{-1}) were used as the reference frequency. The %RDB was calculated according to the equation:

$$\%RDB=100 \times [A_N(C{=}C)_p \times A_N(C\ldots C)_m / A_N(C{=}C)_m \times A_N(C\ldots C)_p]$$

where A_N is the net peak absorbance heights of the polymer (p) and monomer (m) peaks at the corresponding wave numbers.

Statistical Analysis

One-way ANOVA and Tukey's test were used to determine the statistically significant differences in ΔL*, Δa*, Δb*, ΔE and %ΔRDB among the materials tested. Two-way ANOVA and Student-Newman-Keuls multiple comparison tests were used to assess the mean differences in %RDB before and after aging using the type of material and aging status as independent variables. In all cases, an $\alpha=0.05$ level of statistically significant differences was selected. Pearson Product Moment Correlation was used to access the correlation between ΔE and %ΔRDB. Statistical analysis was performed using SigmaStat software (Jandel, St Rafael, CA, USA).

RESULTS

Colorimetry

The results of the color measurements are presented in Table 2. No statistically significant differences were found in ΔL*, Δa* and ΔE among the materials tested ($p<0.05$). The Δb* values in Tetric Ceram demonstrated a statistically significant difference from the rest. Filtek Supreme exhibited a yellow shift (Δb*=+1.06, Δa*=0), Tetric Ceram a green-yellow shift (Δa*=-1.6, Δb*=0.42) and Estelite Σ a blue-green shift (Δb*=-2.68, Δa*=-0.5), with the two latter materials also showing an increase in lightness (ΔL*).

Degree of Cure

Figures 1 through 3 show representative FTIR spectra of unset, set and aged specimens. The results of the %RDB measurements are given in Table 3. Two-way ANOVA revealed a statistically significant interaction between the materials and aging ($p<0.001$). The Student-Newman-Keuls multiple comparison test documented statistically significant differences within each material group before and after aging ($p<0.05$). Among the material groups, Filtek Supreme exhibited the lowest %RDB before aging and Tetric Ceram exhibited the lowest %RDB after aging ($p<0.05$). The %ΔRDB

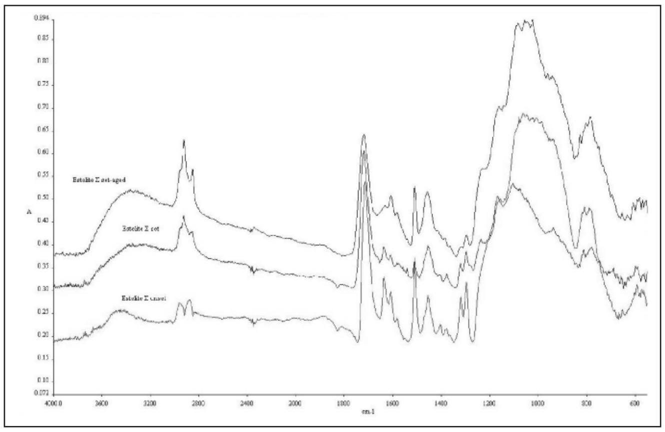

Figure 1. *Representative FTIR spectra of unset, set and aged specimens of Estelite Σ.*

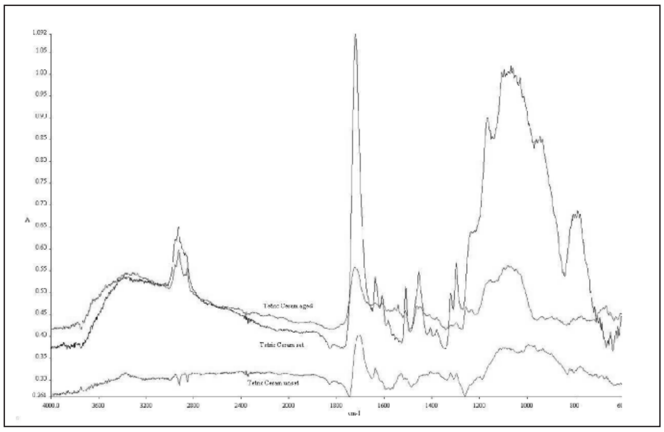

Figure 2. *Representative FTIR spectra of unset, set and aged specimens of Tetric Ceram.*

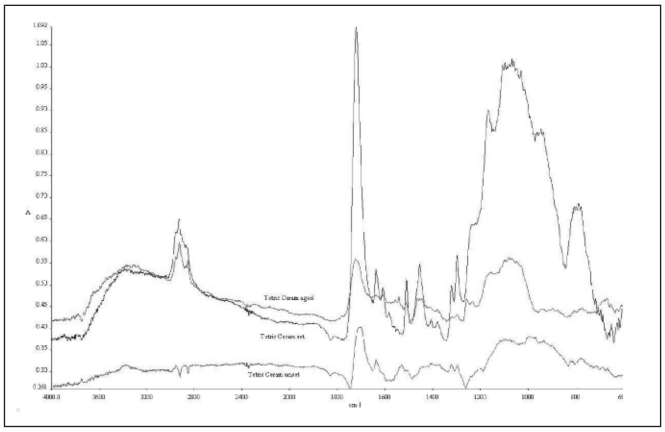

Figure 3. *Representative FTIR spectra of unset, set and aged specimens of Filtek Supreme.*

Table 3: *Results of %RDB Before and After Aging and the Calculated %ΔRDB Values*

Composites	% RDB Before Aging	% RDB After Aging	Δ% RDB
Estelite Σ	54.1±1.5^{a}	39.2±4.3^{c}	14.9±3.1^{e}
Tetric Ceram	52.0±1.7^{a}	31.6±1.8^{c}	20.4±0.7^{f}
Filtek Supreme	44.8±0.3^{b}	38.4±1.1^{c}	6.4±1.1^{g}

Same superscripts indicate mean values with no statistically significant differences before and after aging within and between groups. Same superscripts in %ΔRDB values imply no statistically significant differences ($p<0.05$*).*

values manifested statistically significant differences among all the materials ($p<0.05$). No correlation was found between %ΔRDB and ΔE (r=0.367).

DISCUSSION

According to the results of this study, both parts of the hypothesis were verified. All the materials showed clinically acceptable but visually perceptible ΔE values ($1<\Delta E<3.3$) and a statistically significant reduction in %RDB.

However, there is a controversy regarding the clinically perceptible values of color change (ΔE). Reported values range from 0.4 to 3.7.[18-19] But, in most studies, clinically acceptable values are considered to comply with $\Delta E \leq 3.3$.[4-5,16,20-22]

Many studies have been performed on the color stability of resin composites employing various experimental protocols. In this study, hydrothermal-cycling was combined with photoaging as a means of accelerated aging. Since water plays a major role in monomer leaching, molecular substitution, degradation of the interfacial filler-matrix silane layer and filler particles[23] that affect the color parameters of the restorations,[16] water and temperature conditioning of the samples was included as a sequential treatment to photoaging. Nevertheless, this experimental design does not allow for the drawing of conclusions on the specific effects of hydrothermal-cycling or photoaging on color change.

In general, hydrothermal-cycling results in color changes of resin composites within clinically acceptable limits ($\Delta E<3.3$).[1] As photoaging is considered more aggressive than water storage in color stability testing,[3] it follows that the effect of hydrothermal-cycling in this study is essentially within the clinically acceptable ΔE limits as well. Accelerated photoaging has been shown to provoke a significant increase in Δb* in direct and indirect light-cured composite restorations.[3,18]

In the current study, Filtek Supreme exhibited a yellow shift, Tetric Ceram a green-yellow shift and Estelite Σ a blue-green shift, with the two latter materials showing an increase in lightness. Residual camphorquinone (photoinitiator) has been considered to be responsible for the yellow color shifts over time.[4] Furthermore, tertiary aromatic amines (accelerators) are known to form photoreactive by-products that tend to cause yellow to red/brown discoloration under the influence of light or heat.[3,24] Therefore, differences in the concentration and structure of the photoinitiators and reducing amines may explain the wide spectrum of Δb*and Δa* values obtained among the materials tested.

Apart from catalyst systems, the resin composition, type and size of fillers influence the color stability of tooth-colored restorative materials.[25] Partial substitution of TEGDMA for urethane dimethacrylate (UDMA) comonomer in BisGMA/ TEGDMA resin matrix has been shown to reduce water uptake and stain susceptibility. Water uptake in BisGMA-based resins has been found to increase proportionally to TEGDMA concentration.[26] This leads to a change in stain susceptibility, which is expressed primarily by changes in L* values rather than a* and b* values.[8] However, according to Dietschi and others and Vichi and others,[5,9] differences in the filler-resin ratio and, consequently, variations in water sorption, could not explain the high ΔE values of composite materials alone, since filler size is also implicated in color stability, with a the greater size being more susceptible to water aging discoloration. A possible explanation might be the direct relationship between color perception and scattering, because hydrolytic degradation of the particle-resin matrix interface can modify the way that light is scattered by the particles.[5]

According to the results of this study, Estelite Σ, a BisGMA/TEGDMA resin composite, showed the highest mean ΔE value but with no statistically significant difference from Tetric Ceram, a BisGMA/UDMA/ TEGDMA resin. Possibly, the increased filler volume fraction of Estelite Σ (Table 1) may counterbalance the documented increased water uptake of its resin matrix compared to Tetric Ceram. The excessive blue shift of Estelite Σ may be attributed to the increased translucent scattering in the material, which is designed to provide a chameleon effect that matches the performance of enamel or incisal shades (negative b* and low L* values).[25]

Filtek Supreme, containing DUDMA and BisPMA monomers, both of which are less hydrophilic than BisGMA and TEGDMA,[26] and nanomer and nanocluster fillers, showed the least susceptibility to discoloration, although it exhibited the lowest filler volume content. However, an interesting finding was that Filtek Supreme manifested the lowest %RDB before aging and the lowest %ΔRDB after aging. As the color stability of composite materials is influenced by monomer conversion,[11] the highest conversion of Filtek Supreme before aging may result in a more stable network with fewer changes after aging and therefore improved color stability.

It has been shown that composites containing more than 35% of unconverted C=C bonds tend to be highly susceptible to discoloration.[12] In the current study, the %RDB values obtained before aging ranged from 44.4% to 55.8%, which is in agreement with previous findings.[27] Photoaging of the composites induced a significant amount of post-setting conversion (6.4% to 16.4%), which is inversely related to the %RDB values before aging, apparently due to reduced mobility of the residual C=C bonds in materials with a high initial conversion (steric hindrance). Since photoaging was performed immediately after hydrothermal-cycling (an approximate 11-hour delay), it seems reasonable to expect that free radicals were available to initiate a post-setting conversion.[28] However, the extent to which the residual C=C bonds, after photoaging, are converted to an additional crosslinked network or, in the presence of atmospheric oxygen and UV radiation, are oxidized; promoting production of yellow compounds is not known.[29]

CONCLUSIONS

Color changes were observed after composite aging, leading to visually perceptible ($\Delta E>1$) but clinically acceptable results for all the materials tested ($\Delta E<3.3$). No statistically significant differences were found in color parameters (ΔL^*, Δa^*, ΔE) among the materials tested, except for Tetric Ceram in Δb^*.

Filtek Supreme showed the lowest %RDB before aging and Tetric Ceram showed the lowest %RDB after aging ($p<0.05$). The %ΔRDB values were statistically significantly different among all the materials tested.

No correlation was found between %ΔRDB and ΔE.

(Received 25 September 2006)

References

1. Lee YK, Lim B-S, Kim C-W & Powers JM (2001) Color characteristics of low-chroma and high-translusence dental resin composites by different measuring modes *Journal of Biomedical Materials Research* **58(6)** 613-621.
2. Hosoya Y (1999) Five-year color changes of light-cured resin composites: Influence of light-curing times *Dental Materials* **15(4)** 268-274.
3. Janda R, Roulet JF, Latta M, Steffin G & Rüttermann 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.
4. Kolbeck C, Rosentritt M, Reinhold L & Handel G (2006) Discoloration of facing and restorative composites by UV-irradiation and staining food *Dental Materials* **22(1)** 63-68.
5. 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.
6. Lee YK, El Zawahry M, Noaman KM & Powers JM (2000) Effect of mouthwash and accelerated aging on the color stability of esthetic restorative materials *American Journal of Dentistry* **13(3)** 159-161.
7. Stober T, Gilde H & Lenz P (2001) Color stability of highly filled composite resin materials for facings *Dental Materials* **17(1)** 87-94.
8. Bagheri R, Burrow MF & Tyas M (2005) Influence of food-simulating solutions and surface finish on susceptibility to staining of aesthetic restorative materials *Journal of Dentistry* **33(5)** 389-398.
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(6)** 353-362.
10. Park YA, Chae KH & Rawls HR (1999) Development of a new photoinitiation system for dental light-cured composite resins *Dental Materials* **15** 120-127.
11. Matsumura H, Nakamura M, Tanoue N & Atsuta M (2000) Clinical evaluation of an urethane tetramethacrylate-based composite material as a prosthetic veneering agent *Journal of Oral Rehabilitation* **27(10)** 846-852.
12. Reinhardt KJ (1991) Uncoverted double bonds and interface phenomena in composite materials *Deutsche Jahnartzliche Zeitung* **46(3)** 204-208.
13. Peutzfeldt A & Assmussen E (2000) The effect of post curing on quantity of remaining double bonds, mechanical properties, and *in vitro* wear of two resin composites *Journal of Dentistry* **28(6)** 447-452.
14. Palin WM, Fleming GJ, Burke FJ, Marquis PM & Randall RC (2003) Monomer conversion versus flexure strength of a novel dental composite *Journal of Dentistry* **31(5)** 341-351.
15. Ruyter IE, Nilner K & Möller B (1987) Color stability of dental composite resin materials for crown and bridge veneers *Dental Materials* **3(5)** 246-251.
16. Um CM & Ruyter IE (1991) Staining of resin-based veneering materials with coffee and tea *Quintessence International* **22(5)** 377-386.
17. Seghi RR, Hewlett ER & Kim J (1989) Visual and instrumental colorimetric assessments of small color differences on translucent dental porcelain *Journal of Dental Research* **68** (12) 1760-1764.
18. Setz J & Engel E (1997) *In vivo* color stability of resin-veneered telescopic dentures: A double blind pilot study *Journal of Prosthetic Dentistry* **77(5)** 486-491.
19. Johnston WM & Kao EC (1989) Assessment of appearance match by visual observation and clinical colorimetry *Journal of Dental Research* **68(5)** 819-822.
20. Ferracane JL, Moser JB & Greener EH (1985) Ultraviolet light-induced yellowing of dental restorative resins *Journal of Prosthetic Dentistry* **54(4)** 483-487.

21. Inokoshi S, Kataumi M, Pereira PN, Yamada T & Tagami J (1996) Appearance of composite resins in posterior teeth In: *Factors Influencing the Quality of Composite Restorations. Theory and Practice* Dondi dall'Orologio and Prati C (eds), SATE, Bergamo 141-154.

22. Kim HS & Um CM (1996) Color differences between resin composites and shade guides *Quintenssence International* **27(8)** 559-567.

23. Söderholm K-J (2003) Degradation mechanisms of dental resin composites In: *Dental Materials In Vivo*: *Aging and Related Phenomena* Eliades G, Eliades T, Brantley W & Watts DC (eds) Chicago Quintessence Publishing Co 99-124.

24. 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.

25. 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.

26. Kalachandra S & Terner DT (1987) Water sorption of polymethacrylate networks: bis-GMA/TEGDMA copolymers *Journal of Biomedical Materials Research* **21(3)** 329-338.

27. Silikas N, Kavvadia K, Eliades G & Watts D (2005) Surface characterization of modern resin composites: A multitechnique approach *American Journal of Dentistry* **18(2)** 95-100.

28. Burtscher P (1993) Stability of radicals in cured composite molecules *Dental Materials* **9(4)** 218-221.

29. Sham AK, Chu FC, Chai J & Chow TW (2004) Color stability of provisional prosthodontic materials *Journal of Prosthetic Dentistry* **91(5)** 447-452.