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## Procjena stabilnosti boje svjetlosno i samopolimerizirajućih kompozita nakon ubrzanog starenja

### Color Stability Assessment of Light and Self-Cured Composites Following Accelerated Aging

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#### Sažetak

Svrha istraživanja bila je izmjeriti i usporediti unutarnju stabilnost boje triju svjetlosnopolimerizirajućih materijala i jednoga kemijski stvrdnjavajućeg nakon njihova ubrzanog starenja. **Materijali i metode:** Testovi za stabilnost boja obavljani su na svjetlosnopolimerizirajućim kompozitima – nanopunjenju *Filtek Supreme XT* (3M ESPE), nanohibridu *Tetric Evo Ceram* (Ivoclar Vivadent) i mikrohibridu *Herculite XRV* (Kerr) te na samopolimerizirajućem kompozitu *Bisfil II* (Bisco). Svi uzorci bili su uronjeni u destiliranu vodu (37°C) i držani u tamnoj posudi 24 sata. Nakon toga podijeljeni su u tri skupine. Postupak ubrzanog starenja proveden je prema dvama protokolima – u vodenoj kupelji na 60°C i prema ISO-u 7491. Uzorci iz kontrolne skupine držani su u destiliranoj vodi 30 dana na temperaturi od 37°C. Razlike u boji – ΔE, računale su se iz koordinata CIE L\*a\*b\* izmjerenih spektrofotometrom nasuprot bijeloj pozadini prije postupka starenja uzoraka i poslije njega. Razina osjetljivosti boje postavljena je na 1, a prihvatljivi šum na 3,5. Statistička analiza obavljena je uparenim t-testom i ANOVA-om (p<0,05). **Rezultati:** Svi ispitani materijali pokazali su klinički neprihvatljive promjene boje nakon ubrzanog starenja u vodenoj kupelji, a fotostarenjem nastala je vidljiva promjena boje kod svih svjetlosnopolimerizirajućih kompozita. Nanokompozitni materijali značajno su promijenili boju i u kontrolnoj skupini. **Zaključak:** Unutarnja stabilnost boje testiranih materijala ovisi o uvjetima starenja i vrsti dentalnog kompozita. Kemijski stvrdnjavajući kompoziti pokazali su tijekom fotostarenja bolju stabilnost.

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#### Ključne riječi

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#### Uvod

Stabilnost boje svih dentalnih materijala vrlo je važna za dobar izgled i zadovoljstvo pacijenata. Istaknimo da su zubni kompoziti najčešće korišteni estetski restaurativni materijali. Za razliku od keramike, oni se s vremenom mijenjaju zbog osjetljivosti boje, svojstava materijala i starenja. Kako su im kemijski sastavi i mikrostrukture drugačiji, svi se oni, u nepovoljnim uvjetima okoliša, razlikuju u stabilnosti boje. Jedan od čimbenika koji uzrokuje tu promjenu jest i polimerizacija kompozita. Može se potaknuti kemijski, korištenjem plavog svjetla i dvojako – kemijski i svjetlosno. U dosadašnjim istraživanjima dokazano je da su kemijskopolimerizirajući (CC) kompoziti svjetlosno manje stabilni (1, 2) u odnosu na one svjetlosnopolimerizirajuće (LC). Ta su istraživanja uglavnom i bila razlog da su se u estetskoj dentalnoj medicini LC-i zamijenili CC-ima (3). Ipak, CC-i s optimalnim mehaničkim svojstvima i dalje su poželjna estetska alternativa u nekim zemljama u razvoju, i to zbog financijskih razloga. Tako je *Bisfil II* (BIS) CC-kompozit koji se zadržao na tržištu u zemljama

#### Introduction

Color stability of each dental material is one of the most important aspects of pleasing look and satisfaction of patients. Resin composites are the most widely used esthetic restorative materials. However, unlike ceramics, dental composites change their look over the time due to their color susceptibility, material properties and aging. As to the differences in their chemical composition and physical microstructure all composites vary in color stability after unfavorable environmental changes.

Polymerization of composites is one of the factors which induce color changes. It can be initiated chemically, using blue light or with dual-curing (chemically and by light). Earlier studies showed that chemically-cured (CC) composites compared to light-cured (LC) composites, entail considerably lower color stability (1, 2). This was mainly the reason why LC resin composites largely replaced CC composites in esthetic dental applications (3). Despite this disadvantage, CC composites with optimal mechanical properties are still

poput Bosne i Hercegovine. Do sada, ni prema kojem protokolu, nije ispitana stabilnost njegove boje.

Pretpostavlja se da BIS starenjem (ne zaboravimo, to je razmjerno moderan CC-kompozit) neće značajnije promijeniti boju od svjetlosnopolimerizirajućih kompozita prisutnih na istom tržištu. To bi moglo propagirati uporabu CC-kompozita kao još uvijek dobre estetske alternative za restauracije, barem u postkaninom području.

Svrha ovog istraživanja bila je usporediti unutarnju stabilnost boje triju strukturno različitih LC-kompozita s CC-kompozitnim materijalom nakon ubrzanog starenja i ustanoviti jesu li CC-i estetski kompetitivni s modernim LC-ima.

## Materijali i metode

### Priprema uzoraka

Za ovo istraživanje odabrani su jedan kemijski stvrdnjavajući kompozit – *Bisfil II* (BIS) i tri LC-kompozita – *Filtek Supreme XT* (FS XT), *Tetric Evo Ceram* (TEC) i *Herculite XRV* (HER) u nijansama *A 2* (U). Svojstva tog materijala navedena su u tablici 1. Tijekom pripreme uzoraka za testi-

desired esthetic alternative in some developing countries due to economic limitations. One of CC composites that kept his place on the market of those countries, such as Bosnia and Herzegovina is *Bisfil II* (BIS). Color stability of this composite was not tested earlier according to different protocols. It is assumable that the aging of BIS, which is relatively modern CC composite, would not cause stronger discoloration than the aging of light cured composites present on the same market. This could propagate that use of CC composites could still be acceptable esthetic alternative for the restorations of at least postcanine teeth.

The objective of this study was to compare internal color stability of three structurally different light cured composites with one chemically bonded composite material following accelerated aging and to determine if these materials are esthetically competitive with modern LC materials.

## Materials and Methods

### Preparation of Samples

One chemically-cured composite, *Bisfil II* (BIS) and three light-cured composites, *Filtek Supreme XT* (FS XT), *Tetric Evo Ceram* (TEC), *Herculite XRV* (HER) in shades *A2* (U) were selected for this study. Characteristics of the materials are provided in Table 1.

Tablica 1. Parametri materijala korištenog u ovom istraživanju  
Table 1 Product parameters of the composites used in this study

| Materijal • Product      | Šifra • Code | Proizvođač • Manufacturer                    | Nijansa • Shade | Broj serije • Batch number | Veličina punila u $\mu\text{m}$ • Filler size in $\mu\text{m}$ | Težina punila u % (wt) • Filler weight in % (wt) | Tip i način stvrdnjavanja • Type and Curing mode |
|--------------------------|--------------|--|-----------------|----------------------------|--|--|--|
| <b>Tetric Evo Ceram</b>  | TEC          | Ivoclar Vivadent, Schaan, Liechtenstein      | A2              | M25921, N06133             | 0.04–0.55  | 75–76 %  | nanohibrid (lc) • Nanohybrid (lc)                |
| <b>Filtek Supreme XT</b> | FS XT        | 3M ESPE, St. Paul, SAD • USA                 | A2 D            | N102321                    | 0.02 and 0.6–1.4   | 78.5 %   | nanopunilo (lc) • Nanofilled (lc)                |
| <b>Herculite XRV</b>     | HER          | Kerr Italia, S.r.l, Scafati, Salerno, Italia | A2 D            | 3316843, 3366208 14546     | 0.6  | 79 %   | mikrohibrid (lc) • Microhybrid (lc)              |
| <b>Bisfil II</b>         | BIS          | Bisco Inc. Schaumburg, SAD • USA             | U               | 1000003854                 | 0.04–5.0   | 84% base; 83% cat                                | samostvrdnjavajući • autocured                   |

ranje koristili smo se plastičnim kalupom 10 x 2 mm. Materijal je stavljen u kalup ispod kojega su bili mikroskopsko predmetno stakalce i celuloidna vrpca (*Mylnar*). Zatim je napunjeni kalup prekriven folijom *Mylnar* i komprimiran drugim milimetar debelim predmetnim stakalcem. To je omogućilo ravnomjernu polimerizaciju svakog diska s jednakom udaljenošću od izvora svjetla, pa se postigla glatka i ravna površina kompozita (4). Višak materijala istisnut je predmetnim stakalcem sprječavajući stvaranje zračnih mjehurića (5). Ukupno su bila pripremljena 52 uzoraka, tj. trinaest za svaki kompozitni materijal. Polimerizacija svjetlosnopolimerizirajućeg materijala trajala je 20 sekundi, a obavljena je snagom od 1200 mW/cm<sup>2</sup> uređajem *Elipar™ FreeLight 2 LED Curing Light* (3M ESPE, St. Paul, MN, SAD). Jakost svjetiljke za polimerizaciju provjeravala se radiometrom (Bluephase Meter (Ivoclar Vivadent, Schaan, Liechtenstein, ser. no. 003546) odmah nakon polimerizacije svake skupine od pet uzoraka.

A 10 x 2mm plastic mold was used to prepare samples for testing. The material was placed into the mold under which a microscopic plate was placed covered by the celluloid (*Mylar*) strip. The mold was filled with the material, covered with the Mylar strip and pressed against using another 1 mm thick plate. This effectively ensured that polymerization of each disc was at equal distance from the light source and that the sample surface of the composites equally flattened (4). Excess material was squeezed out using glass plates making sure no air bubbles were formed (5). Total of 52 samples were prepared, i.e. thirteen per each composite material. The polymerization of the light-cured materials was performed by *Elipar™ FreeLight 2 LED Curing Light* (3M ESPE, St. Paul, MN, USA) with 20s in 1200 mW/cm<sup>2</sup> output. The intensity of the curing lamp was checked with a radiometer *Bluephase Meter* (Ivoclar Vivadent, Schaan, Liechtenstein, Ser. No. 003546) right after every batch of five samples was cured.

Uzorci nisu polirani radi izbjegavanja bilo kakve promjene na površini (4, 5, 6). Kemijski polimerizirani materijal pomiješan je prema uputama proizvođača, stavljen u kalup i pritisnut dvama predmetnim stakalcima. Prije nego što su izvađeni iz kalupa, uzorci su polimerizirani 60 sekundi.

Svi su uzorci 24 sata bili uronjeni u destiliranu vodu (37 °C) i spremljeni na tamno mjesto, a nakon postupka stvrdnjavanja podijeljeni su u tri skupine – dvije eksperimentalne i jednu negativnu kontrolnu.

#### Ubrzani postupak starenja

Ubrzano starenje obavljeno je prema dvama protokolima – ISO 7491 (fotostarenje, Suntest) i Asmussenovu (vodena kupelj). Fotostarenju je bilo podvrgnuto 20 uzoraka (5 diskova od svakog materijala) koji su 14 dana bili uronjeni u destiliranu vodu (37 °C), a zatim su na 24 sata prebačeni u uređaj *Suntest CPS+* (Atlas Materials Test Technology GmbH, Linssengericht, Njemačka) prema protokolu ISO 7491, kako je opisano i u dosadašnjim istraživanjima (7, 8, 9, 10).

Kako bi se postigla ista krajnja točka za sve materijale, nakon fotostarenja provedeno je 15-dnevno dodatno starenje u destiliranoj vodi (37 °C) u kontroliranoj atmosferi. Ostalih 20 uzoraka (5 diskova od svakog materijala) ostavljeno je u destiliranoj vodi (60 °C) četiri tjedna prema Asmussenovu protokolu, a koristila su se i dosadašnja istraživanja (2, 11, 12). Kontrolna skupina (12 uzoraka, 3 diska od svakog materijala) čuvala se 30 dana na temperaturi od 37 °C na tamnom i suhom mjestu.

#### Procjena boje

Vlažni uzorci osušeni su prije određivanja boje umatnjem u celulozu. Boja uzoraka mjerila se spektrofotometrom (Vita Easyshade, Vita Zahnfabrik, Bad Säckingen, Njemačka) korištenjem bijele pozadine od polimernog materijala i CIE-vrijednostima ( $L^*=97,6$ ,  $a^*=0,5$ ,  $b^*=1,6$ ). Kako su pokazali rezultati prijašnjih istraživanja, uređaj pouzdano određuje boju i u standardiziranim i u kliničkim uvjetima (13). Mjerenja su ponovljena tri puta na istom mjestu i zatim je uređaj izračunao srednju vrijednost triju mjerenja ( $L^*a^*b^*$ ). Spektrofotometar je kalibriran prije svakog mjerenja korištenjem integrirane standardne bijele pločice. Stabilnost boje prikazana je razlikom u boji ( $\Delta E$ ) između početne vrijednosti nakon 24 sata ( $L^*_1$ ,  $a^*_1$ ,  $b^*_1$ ) te vrijednosti nakon ubrzanog starenja u usporedbi s kontrolnom skupinom. Daljnja mjerenja boje u prvoj skupini uzoraka obavljena su sedam i četrnaest dana nakon što su stavljeni u destiliranu vodu (37 °C), dva sata nakon završetka testa na Suncu i 30 dana nakon stavljanja u destiliranu vodu (37 °C). Za skupinu u vodenoj kupelji provedena su dodatna mjerenja boje nakon sedam, četrnaest i trideset dana nakon uranjanja u destiliranu vodu (60 °C). Za svaku suhu skupinu sljedeće je mjerenje obavljeno nakon trideset dana.

Promjene boje računale su se formulom:  $\Delta E^* = [(\Delta L^*n)^2 + (\Delta b^*n)^2 + (\Delta a^*n)^2]^{1/2}$ . Vrijednost  $\Delta E^*$ , koja je uzeta kao vidljiva, postavljena je na  $\Delta E^*=1,7$ , a vrijednosti  $\Delta E^*\geq 3,5$  smatrane su klinički neprihvatljivima (14). Statistički analiza obavljena je uparenim t-testom i ANOVA-om ( $p \leq 0,05$ ).

The samples were not polished to avoid any surface modifications (4, 5, 6). Chemically-cured material was mixed according to the manufacturer's instructions, packed into the mold and pressed between the two glass plates. The specimens were cured for 60 min before being removed from the mold. All samples were stored in distilled water in a dark at 37 °C for 24 hours after the curing procedure, and then divided into three groups, i.e. two experimental groups and one negative control group.

#### Accelerated Aging Process

Accelerated aging was carried out in accordance with the two protocols: ISO 7491 (photoaging, Suntest) and Asmussen (water bath). Photoaging involved 20 samples (five discs from each material) stored in distilled water at 37 °C for 14 days and transferred to Suntest CPS+ device (Atlas Materials Test Technology GmbH, Linssengericht, Germany) for 24 hours according to ISO 7491, as in previous studies (7,8,9,10). To obtain the same endpoint for all tested materials, photoaging was followed by additional aging in distilled water and dark at controlled atmosphere at 37 °C for the period of 15 days. Other 20 specimens (five discs for each material) were placed in distilled water at 60 °C for 4 weeks according to the methodology proposed by Asmussen and according to previous studies (2, 11, 12). The control group (12 samples, three discs for each material) was stored in dark and dry environment at 37 °C for the period of 30 days.

#### Color Evaluation

Wet specimens were blot-dried using cellulose wadding before measurement of color was performed. Color of the samples was measured with a spectrophotometer (Vita Easyshade, Vita Zahnfabrik, Bad Säckingen, Germany) using white backing tiles made of polymeric material with CIE values ( $L^*=97,6$ ,  $a^*=0,5$ ,  $b^*=1,6$ ). As the findings of the previous study showed, this device is reliable for color determination in standardized and clinical environments (13). The measurements were repeated three times at the same point and the instrument calculated the mean of three measurements ( $L^*a^*b^*$ ). Prior to every measurement, the spectrophotometer was calibrated using integrated standard white plate. The color stability was indicated by color difference ( $\Delta E$ ) between the initial value after 24 hours ( $L^*_1$ ,  $a^*_1$ ,  $b^*_1$ ) and the values after accelerated aging, respectively compared with the control group. Further color measurements of first group were made after 7 days and 14 days after being placed in distilled water, at 37 °C, 2 hours after completion of Suntest and 30 days after being placed in distilled water at 37 °C. For the water bath group, further color measurements were performed after 7 days, 14 days and 30 days after being placed in distilled water at 60 °C. For the dry group, the following color measurement was made after 30 days.

The color shifts were calculated using the formula  $\Delta E^* = [(\Delta L^*n)^2 + (\Delta b^*n)^2 + (\Delta a^*n)^2]^{1/2}$ . The value of  $\Delta E^*$ , which was taken as perceptible was  $\Delta E^*=1,7$ , while values of  $\Delta E^*\geq 3,5$  were considered as clinically unacceptable (14). Statistical tests conducted to analyze values obtained included paired t-test and ANOVA ( $p \leq 0,05$ ).

## Rezultati

Rezultati mjerenja boje ( $\Delta E^*$ ) iz skupina testa Sunca (skupina 1) i vodene kupelji (skupina 2) nalaze se u tablicama 2. i 3. U sklopu protokola testa Sunca (Sunset) svi ispitani uzorci promijenili su boju iznad granice uočljivosti (tablica 2.). Svi ispitani materijali imali su klinički neprihvatljivu promjenu boje nakon ubrzanog starenja u vodenoj kupelji (tablica 3.). FS XT pokazao je neprihvatljivu promjenu boje već nakon sedam dana, a najuočljivija promjena zabilježena je 30 dana nakon testiranja.

Promjena boje TEC-a bila je klinički vidljiva, ali prihvatljiva poslije prvih sedam dana u vodenoj kupelji. Nagla promjena dogodila se sedmog i četrnaestog dana, nakon čega se smanjila. Kod HER-a je promjena boje bila vidljiva već nakon sedam dana testiranja, a neprihvatljiva promjena pojavila se nakon četrnaest dana. Kod BIS-a je promjena boje bila vidljiva nakon samo sedam dana u vodenoj kupelji, a neprihvatljiva promjena nakon četiri tjedna. U kontrolnoj skupini vidljiva promjena boje počela je kod nanokompozita (tablica 4.), a vrijednosti ostalih dvaju materijala ostale su ispod prihvatljivih vrijednosti *in vivo*.

## Results

The results of the color measurements ( $\Delta E^*$ ) from the Suntest group (Group 1) and the water bath (Group 2) are provided in Tables 2 and 3. According to the Suntest protocol, all materials tested changed their color beyond the perceptibility threshold (Table 2). All materials tested showed clinically unacceptable color changes after accelerated aging in water bath (Table 3). FS XT showed unacceptable results in the water bath after only 7 days, whereas the most noticeable color change became apparent 30 days into the test. Color change of TEC was clinically visible but acceptable after initial 7 days in the water bath. A sudden color change occurred between 7th and 14th day and then material discoloration decreased. HER showed perceptible color differences after only 7 days into the test, whereas unacceptable discoloration occurred after 14 days. BIS showed perceptible change in water bath after only 7 days and unacceptable differences after 4 weeks. The control group reported visible color changes for nano-composites (Table 4.), while the control group values for the other two materials remained within *in vivo* acceptable values.

**Tablica 2.**  $\Delta E$  vrijednosti testiranih materijala u sunset skupini između dvaju vremenskih razdoblja  
**Table 2**  $\Delta E$  values of materials tested in Sunset group between the two given periods

| $\Delta E$ | FS XT |      |      |      | BIS  |      |      |      | HER  |      |      |      | TEC  |      |      |      |
|------------|-------|------|------|------|------|------|------|------|------|------|------|------|------|------|------|------|
|            | 1 d   | 7 d  | 14 d | sun  | 1 d  | 7 d  | 14 d | sun  | 1 d  | 7 d  | 14 d | sun  | 1 d  | 7 d  | 14 d | sun  |
| 7 d        | 1.02  |      |      |      | 1.27 |      |      |      | 0.38 |      |      |      | 0.67 |      |      |      |
| 14 d       | 1.81  | 0.9  |      |      | 1.58 | 0.73 |      |      | 0.53 | 0.79 |      |      | 1.13 | 0.97 |      |      |
| sun        | 2.98  | 2.28 | 1.46 |      | 5.48 | 4.92 | 4.22 |      | 5.27 | 5.21 | 5.35 |      | 3.4  | 3.48 | 2.57 |      |
| 30 d       | 3     | 2.04 | 1.19 | 1.16 | 3.56 | 2.83 | 2.14 | 2.13 | 4.51 | 4.48 | 4.58 | 0.85 | 2.7  | 2.78 | 1.91 | 0.72 |

**Tablica 3.**  $\Delta E$  vrijednosti testiranih materijala u vodenoj kupelji između dvaju vremenskih razdoblja  
**Table 3**  $\Delta E$  values of materials tested in water bath between the two given periods

|      | $\Delta E$ FS XT |      |      | $\Delta E$ BIS |      |      | $\Delta E$ HER |      |      | $\Delta E$ TEC |       |      |
|------|------------------|------|------|----------------|------|------|----------------|------|------|----------------|-------|------|
|      | 24h              | 7 d  | 14 d | 24h            | 7 d  | 14 d | 24 h           | 7 d  | 14 d | 24 h           | 7 d   | 14 d |
| 7 d  | 7.89             |      |      | 2.55           |      |      | 1.79           |      |      | 2.07           |       |      |
| 14 d | 10.61            | 3.37 |      | 2.51           | 2.07 |      | 4.29           | 3.19 |      | 12.93          | 11.65 |      |
| 30 d | 14.96            | 8.09 | 4.72 | 4.53           | 3.24 | 3.03 | 9.15           | 8.77 | 6.05 | 14.75          | 13.7  | 3.14 |

**Tablica 4.**  $\Delta E$  vrijednosti testiranih materijala u kontrolnoj skupini nakon 30 dana  
**Table 4**  $\Delta E$  values of materials tested in the control group after 30d

| Kontrolna skupina •<br>Control group | $\Delta E$ |
|--------------------------------------|------------|
| FS XT                                | 5.58       |
| TEC                                  | 24.97      |
| HER                                  | 2.64       |
| BIS                                  | 0.63       |

## Rasprava

U nekim zemljama u razvoju moderni svjetlosnopolimerizirajući kompoziti nisu uvijek financijski prihvatljivi. Unatoč tomu pacijenti zahtijevaju bolju estetiku nego što se može postići amalgamskim ispunima. Neki od novijih kemijski stvrđavajućih kompozita imaju povoljna mehanička svojstva i vrlo dobru početnu boju. No ima mišljenja da ti materijali znatnije mijenjaju boju nego suvremeni LC-kompoziti. U našem istraživanju usporedili smo stabilnost boje kemij-

## Discussion

In some developing countries modern, light cured composites are not always economically acceptable. Nevertheless patients seek better esthetics than it can be achieved with amalgam restorations. Some newer chemically cured composites have favorable mechanical properties and initially very good color. However, believe exists that these materials discolor more strongly than the modern light cured composites. In this study color stability of chemically bounded

ski vezujućih kompozita koje rabe dentalni liječnici u nekim zemljama u razvoju, sa stabilnošću boje različitih LC-a. Korištene su *in vitro* metode ubrzanog starenja materijala za simulaciju učinka produženog izlaganja okolišnim uvjetima. Premda ti uvjeti ne mogu replicirati složeni *in vitro* okoliš, omogućuju procjenu potencijala restorativnog materijala kad je riječ o kliničkoj stabilnosti boje (15). Starenje u vodenoj kupelji korišteno je kao mjerni test za stabilnost boje kompozita (6, 11). Dobiveni rezultati odgovaraju 12-mjesečnom starenju na temperaturi od 37 °C (1). Metoda testiranja za unutarnju stabilnost boje fotostarenjem uključivala je 24-satno ksenonsko svjetlo prema protokolu ISO 7491:2000. Dobiveni rezultati ne mogu se usporediti s određenim vremenom *in vivo* (17) te su zbog osiguravanja iste krajnje točke uzorci suhe grube i one izložene fotostarenju također skladišteni 30 dana u vodi na temperaturi od 37 °C (9, 10). Dobiveni rezultati (tablica 3.) pokazuju da je starenje u vodenoj kupelji rezultiralo većom promjenom boje negoli starenje pod ksenonskim svjetlom (tablica 2.). Ta nestabilnost boje u vodenoj kupelji slaže se s istraživanjima Asmussena (11) te Vichija i suradnika (6). Promjena boje kompozita u vodenoj kupelji tijekom vremena (tablica 3.) također se slaže s prijašnjim istraživanjima (5, 12). Promjena boje u postupku ubrzanog starenja događa se zbog degradacije i uglavnom se pripisuje difuziji boje u smolu (18). Starenje kompozita u vodi ovisi o vremenu i proporcionalno je apsorpciji vode (19). U ovom je istraživanju iznos promjene boje pri ubrzanom starenju ovisio o vrsti materijala, što se slaže s dosadašnjim studijama (20). Rezultati istraživanja pokazuju da je fotostarenje rezultiralo najvećim promjenama boje tijekom 24-satnog osvjetljenja (tablica 2.), a starenje u vodenoj kupelji imalo je manju ulogu u promjeni boje. To je potvrđeno i u drugim istraživanjima (7, 9, 21). Pretpostavlja se da ksenonsko svjetlo iz uređaja *Sunset* djeluje kao inicijator polimerizacije na preostale nepolimerizirane fotoinicijatore (22), pa bi takva polimerizacija mogla objasniti brzu promjenu boje nakon fotopolimerizacije.

Kamforokinin (CQ) je najčešće korišteni inicijator u LC-kompozitima, a kod CC-kompozita to je aromatski tercijarni amin. Moderni kompoziti CQ dodatno sadržavaju manje količine drugih fotoinicijatora s apsorpcijskim rasponima oko 400 nm (8, 22). LED-uređaji za polimerizaciju emitiraju svjetlo valne duljine od 430 do 480 nm, što je optimalni spektar za transformaciju CQ-a u bezbojnu molekulu nakon 20 sekundi osvjetljavanja (22), ali ne pokriva njegov cijeli apsorpcijski raspon (380 – 510 nm, maks. 468 nm). Promjena boje može biti posljedica nepodudaranja emitiranog svjetlosnog spektra iz polimerizacijskih svjetiljki i apsorpcijskog spektra fotoinicijatora (23).

Nanokompoziti su pokazali najmanje stabilnu boju u vodenoj kupelji i znatno su se promijenili i na tamnom mjestu i u suhim uvjetima, te je njihova promjena boje bila veća od one kod mikrohibridnih kompozita. To se slaže s prijašnjim istraživanjima na nanokompozitima u kojima se ističe da se oni degradiraju više nego mikrohibridni kompoziti ako se dugo drže u vodi (24).

Može se očekivati da su kemijski stvrdnjavajući kompoziti podložniji promjeni boje zbog vrste inicijatora i prazni-

composite, used in some developing countries was compared with the color stability of different light cured composites.

*In vitro* methods of accelerated aging were used to simulate the effect of prolonged exposure of some environmental conditions to the materials. Although these conditions cannot replicate complex *in vivo* environment, they allow us to assess potential of restorative materials for their clinical color stability (15). Aging in water bath was assessed as the reference test for color stability of composites (6, 11). The results obtained correlate with 12 months aging on 37 °C (1). Test methods relevant for internal color stability evaluation was accelerated photoaging using xenon light for 24 hours following ISO 7491:2000. However the results cannot be correlated with the specific time frame *in vivo* (17). Therefore, in order to ensure the identical ultimate moment for all materials tested and experimental protocols, samples of dry group and those exposed to photoaging were also stored in water at 37 °C up to 30 days (9, 10).

Results showed (Table 3) that aging in water bath resulted in discoloration to a greater extent compared to aging under the xenon light (Table 2). This color instability in water bath was consistent to the studies of Asmussen (11) and Vishi et al. (6). Composites in water bath reported color change that increased over time (Table 3), which also corresponds to the earlier studies (5, 12). Color changes under accelerated aging process occurred as a result of degradation, mainly attributed by diffusion of water into the resin (18). Aging of composites in water was time dependent and proportional to the absorption of water (19). In the present study the extent of color change due to accelerated aging depended on the type of material, which is in accordance with previous reports (20).

The results of this study showed that photoaging induced largest color changes during the illumination period of 24 hours (Table 2), whereas aging in water alone had a minor role in discolorations as confirmed with other findings (7, 9, 21). If assumed that Xenon light from Suntest device was a polymerization initiator for uncured additional photoinitiators (22), then postpolymerisation could explain color change occurrence of color change following photocuring.

Camphorquinone (CQ) is mostly used as an initiator in the light-cured (LC) composites, while chemically-cured (CC) composites involve aromatic tertiary amines as an initiator of polymerization. In addition to CQ, modern composites contain minor amounts of other photoinitiators with absorption range of close to 400 nm (8, 22). LED lamp mostly emits light with wavelength of 430-480 nm, which is optimal for the transformation of the emission spectrum of camphorquinone to colorless substances following irradiation of 20 s (22), but it does not cover the entire absorption range of CQ (380-510nm, max. 468 nm). The color shift could be caused with mismatching of the light spectrum emitted from curing lamp and the absorption spectrum of photoinitiators (23).

Nano-composites showed the least stable color in the water bath and they also significantly changed in dark and dry conditions. Discoloration was expressed to a greater extent relevant to microhybrid composites. This was consistent with earlier research which showed that nano-composites can de-

na ispunjenih zrakom koji se utiskivao u materijal tijekom ručnog miješanja dviju pasta. Kod starenja u vodenoj kupelji CC-kompoziti su pokazali veću stabilnost nego tri LC-materijala testirana u ovom istraživanju. Zaključci ovog istraživanja slažu se s dosadašnjim istraživanjima u kojima se ističe da nakon ubrzanog starenja BIS ima najstabilniju boju među nekoliko samostvrdnjavajućih CC-kompozita (18). To se može objasniti tvrdnjama u dosadašnjim istraživanjima u kojima se razlika u promjeni boje kod kemijski stvrdnjavajućih (CC) kompozita pripisuje različitim aktivatorima (2).

Kod testiranih materija razlikuju se veličina čestica i vrsta punila (tablica 1.), a veličina čestice ima važnu zadaću u procesu degradacije kompozita. Veća degradacija kompozita s nanočesticama punila, nakon starenja u vodenoj kupelji, može se pripisati veličini čestica. Vodeni medij prekinuo je spoj punilo/matriks, što je uzrokovalo istjecanje nanočestica iz nanokompozita jer su molekule vode također nanovećane. Može se pretpostaviti da male čestice u nanokompozitima imaju veće površinske veze s matriksom, što povećava apsorpciju vode i rezultira degradacijom dijelova punila i matriksa (19). U nekim se istraživanjima promjena boje nanokompozita u vodenoj kupelji objašnjavala poroznošću između čestica punila (25) koja nastaje kao rezultat ekspulzije nanofilera iz nanoklastera (26). Malene nanomolekule, kada se stave u vodu, mogu se brže isprati nego veće molekule koje se nalaze u sklopu drugih dvaju testiranih kompozita, pa tako nastaje porozni materijal ispunjen vodom. Promjena boje TEC-a u vodenoj kupelji može se objasniti ako se uzme u obzir da taj materijal ima protukarijesni učinak zbog otpuštanja određene količine fluora iz iterbijeva trifluorida (17). Razmjerno mala promjena boje CC-kompozita (BIS) u vodi vjerojatno je povezana s (u sastavu velikim postotkom) anorganskim dijelom i zbog toga manjim upijanjem vode (18). Slično i veći udjel organske komponente kolerira s većom promjenom boje (2).

Ovo je suprotno izvještaju Vichija koji je procjenjivao hibridne kompozite i ustanovio da oni s većim česticama u vodenoj kupelji znatnije mijenjaju boju (6). Količina punila možda nije jedini čimbenik za promjenu boje jer materijali sa sličnim količinama punila različito su mijenjali boju u provedenim protokolima. Materijali s UDMA-om u matriksu u ovom su istraživanju bili podložni većoj promjeni boje u vodenoj kupelji, a prihvatljivu promjenu imali su nakon postupka fotostarenja. Kao što je ustanovljeno u nekim istraživanjima, možda je 24-satno fotostarenje prema standardu ISO 7491 (27) prekratko, a u ovom istraživanju zaključeno je da bi osvjetljenje ksenonskim svjetlom u budućim istraživanjima trebalo produljiti.

## Zaključak

Uz nedavni napredak postignut kod LC-kompozita i pojavljivanja novih univerzalnih nanokompozita, velik dio tržišta i dalje se dijeli sa znatnim brojem CC-kompozita. Zato je

grade more than microhybrid composites in the water long-term holding (24).

It can be expected that chemically bonded composites are more prone to color change due to their photo initiator type and the occurrence of voids, caused by air pushed into the material during hand-mixing of two pastes. After aging in water bath, the CC composite proved to be more stable than the three LC materials used in this study. Findings of this study are consistent to previous findings that BIS proved to entail the most stable color among several self-cured composites following accelerated aging (18). This can be explained by the claim of the previous study whereby the difference in discoloration of chemically-cured composites is prompted by their different activators (2).

Particle sizes and type of filler differ in materials tested (Table 1). The particle size plays a role in degradation process of composites. Higher discoloration of composites with nanoparticles after aging in water bath may be due to their particle size. The aqueous medium ruptured filler/matrix interface, causing nanoparticles flushing from nano-composites, since the water molecules are also nanosized. It could be assumed that the small particles in nano-composites have higher surface area for the interconnection with the matrix, which increases the absorption of water and thus degradation of the compound filler and matrix (19). Previous study reported that discoloration of nano-filled composite in water bath may be induced with porosity between the filler particles (25) that occurs as a result of expulsion of nanofillers from nanoclusters (26). The small nanomolecules, when placed in a water environment could be quickly rinsed than larger, more massive molecules contained within the other two tested composites, creating a porous material filled with water. Discoloration of TEC in water bath can be explained considering that this material has anticariogenic properties due to release a certain amount of F<sup>-</sup> from the ytterbium trifluoride (17). Relatively low discoloration of chemically cured BIS in the water bath is probably associated with its high proportion of the inorganic part, and therefore less water sorption (18). Similarly, higher proportion of organic compound correlates with greater discoloration (2). This was in contrast to Vichy's report who evaluated hybrid type of the composites and found that composites with larger particles have a higher discoloration in water bath (6). However, the amount of filler may not be the only factor in the discoloration process whereas some materials with similar amounts of fillers, different discoloration suffered in protocols conducted. With regard to the matrix, materials from this study containing UDMA suffered greater color change in the water bath, but smaller, acceptable color change after photo aging. As earlier study found that exposure to illumination over 24 hour period according to ISO 7491 was too short (27), findings of this study show that that xenon light illumination should be extended in some future research.

## Conclusions

As a result of recent advances in LC composites and the emergence of the new universal and nano-composites, a substantial number of CC materials continue to take share of

stabilnost boje i dalje imperativ. Glavni čimbenik za promjenu boje kompozita nakon fotostarenja bilo je osvjetljavanje ksenonskim svjetlom. U vodenoj kupelji boja se znatno promijenila kod svih testiranih materijala.

Prijašnja stajališta da se kod CC-kompozita događaju veće promjene boje (28) u ovom istraživanju nisu potvrđena. Naši rezultati upućuju na to da testirani LC-kompoziti nemaju bolju stabilnost boje u odnosu na CC-kompozite. Zato uzrok promjene boje mora biti negdje drugdje, a ne u inicijatorima polimerizacije.

Stabilnost boje testiranih materijala ovisi o vrsti materijala i značajno je varirala ovisno o primijenjenom protokolu ubrzanog starenja. Zato je za ispitivanje stabilnosti boje kompozita potrebno provesti različite protokole kako bi se odredila boja kompozita koja u različitim uvjetima najbolje zadržava unutarnju nijansu.

Na temelju nalaza ovog istraživanja proizvođači bi se trebali potruditi da u buduću poboljšaju optička svojstva svojih CC-kompozita jer mogu ostati dobra alternativa za estetske restauracije u zemljama u razvoju.

the market. Therefore, the importance of their color stability continues to be imperative.

A major factor in changed color of composites following photoaging was xenon light illumination. In water bath aging enormous discoloration of all materials tested occurred.

The earlier claim that self-cured composites show higher discoloration relevant to the light-cured ones (28) was not supported in this study. The results of this study indicate that the LC composites do not entail better color stability relevant to the chemically-cured material tested. Hence, the cause of color change must be sought in other components of the material, and not in the initiator of polymerization.

Color stability of materials tested depended on type of material and enormously varied based on the aging protocol. Therefore, when testing color stability of restorative materials, it is necessary to perform multiple protocols – in order to determine which specific composite effectively entails the most consistent internal color in different conditions. Based on the findings of this research, manufacturers should be prompted to further improve optical properties of their CC composites, as they can remain good alternative for esthetic restorations in developing countries.

#### Abstract

**Objectives:** Measure and compare internal color stability of three light-cured composites and one chemically bonded material after their accelerated aging. **Materials and Methods:** Color stability tests included nano-filled Filtek Supreme XT (3M ESPE), nano-hybrid Tetric Evo Ceram (Ivoclar Vivadent), microhybrid Herculite XRV (Kerr) of light cured and Bisfil II (Bisco) of self cured composites. All samples were immersed in distilled water of 37°C and kept in a dark chamber during 24 hours. Thereafter they were divided into three groups. Accelerated aging was performed in accordance with the two different protocols, i.e. water bath at 60°C and ISO 7491. Control group specimens were stored in distilled water at 37°C for 30 days. Color differences,  $\Delta E$  were calculated from CIE L\*a\*b\* coordinates measured with spectrophotometer against white backing before and after aging of samples. The color perceptibility threshold was set at 1.7 and acceptability threshold at 3.5. Statistical tests carried out on the groups included paired t-test and ANOVA ( $p \leq 0.05$ ). **Results:** All tested materials showed clinically unacceptable color changes after accelerated aging in water bath, whereas photoaging induced perceptible color change in all light-cured composites. Nano-engineered composites significantly changed their color also in the control group. **Conclusions:** Internal color stability of tested materials depends on aging conditions and type of dental composite. Chemically-cured material showed better color stability by photo aging.

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#### Key words

Composite Resins; Aging; Materials Testing; Color

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