

## Color stability and hardness in dental composites after accelerated aging

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### Abstract

**Objectives.** To investigate the color and microhardness changes of five chemically- and five light-curing composites as a function of accelerated aging from light exposure.

**Materials and methods.** From each material five composite specimens were embedded in epoxy resin prior to determining the Knoop microhardness of the surface. For analyzing the color  $\Delta E^* = f((L^* a^* b^*))$  with a spectrophotometer, three discs per composite were prepared. After measuring the baseline for hardness and color the same specimens were exposed to a xenon arc light and water in a Weather-Ometer machine for a total radiant energy of 150 kJ/m<sup>2</sup> and 122 h. The microhardness and the color were again determined following the aging treatment.

**Results.** Each material showed a significant increase in hardness after aging treatment ( $p < 0.05$ ). Comparing the hardness changes (in %) of the light-cured materials with the chemically cured materials, no significant difference could be found. Perceptible color differences could be observed for all the materials. Three brands showed small differences with  $\Delta E^* = 1.6$ – $2.2$ , while four composites had  $\Delta E^*$  ranging from 6.2 to 15.5. A significant correlation between hardness values and color changes could not be established.

**Clinical significance.** The findings suggest that, since light-curable materials showed significantly more resistance to color changes after accelerated aging by light and water than chemically-cured materials, they may be more esthetically acceptable. Color changes were not correlated with surface hardness changes of the materials after aging.

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### 1. Introduction

In the era of esthetic composite restorations, the demand for overall good color stability is increasing [1,2]. Most anterior restorations are replaced because of unacceptable color match [3]. Several sources of discoloration have been suggested. External discoloration can be a result of plaque accumulation involving staining. Another reason is the degradation or staining within the superficial layer of resin composite related to dietary and smoking habits [4–6]. Apparent color differences also may be related to surface roughness from polishing procedures and wear, as well as chemical degradation. Discoloration in the deeper layers of the material can be due to physico-chemical reactions

within the material itself that are shade related [7]. Tertiary amines contribute to discoloration, by a change in hue, from whitish to yellowish appearance [8]. A previous study reported the influence of initiators and activators on the surface hardness after the curing process [9]. The resin composition and conversion [10,11] play major roles and, in addition, it has been shown that water acts as a carrier for staining agents in the water sorption process [12]. Oxygen inhibition at the surface and in porosities may induce staining as well [13].

Composites are formulated with a variety of chemical and structural variations that may be related to their specific applications. In this study light-curing and chemically-curing composites recommended for similar clinical applications from five manufacturers were compared. The materials used in this study were chosen according to the manufacturers' recommendations for the most similar

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filler types and resin in light-curing and chemically-curing products.

Microindentation has been used to evaluate the surface hardness of hard tissue like dentin and enamel [14–18] or bone [19], as well as polymer materials [20–24]. Although hardness of composites has been studied extensively, the relation of discoloration with hardness has received limited attention. In developing countries where rural areas have no access to conventional facilities and lack electricity, the chemically-cured materials are the first choice when anterior restorations are performed. Anterior restorations are especially prone to failure when filled with glass-ionomer cements. Chemically-cured composites, on the other hand, have been used for this purpose and showed better results. Only a few anterior chemically-cured composites are on the market and therefore will be compared to similar light-cured composites. This study evaluates anterior chemically-cured materials to determine if they have adequate characteristics. In addition, they were compared to similar light curing formulations.

The aim of this study was to determine the color and microhardness changes of chemically- and light-curing composites as a function of accelerated aging from light exposure and water spray. The hypothesis tested was that composites with higher hardness values have less color changes than composites with lower hardness and that hardness increases after the aging treatment. The latter is based on a previous study [23] showing that post-cure heat treatment improved toughness, hardness, and flexural modulus, predominantly as a result of the degree of cure within the composite. Considering the aging treatment as an extrinsic post-curing factor, it is expected that hardness will increase after aging and that the materials with higher baseline hardness will have better color stability.

## 2. Materials and methods

Five chemically (cc) and five light-cured (lc) composites from five companies were selected for this study. Characteristics of the materials are given in Table 1. In an attempt to simplify comparisons, shades A2 or U (universal) were selected for all materials, but color differences among products and manufacturers were still perceptible. According to the manufacturers, the light- and chemically-cured materials either have the same filler and/or resin composition or very similar compositions, suggesting a basis for comparison of the material groups. Precise formulations of these composites were not provided by the manufacturers.

### 2.1. Knoop hardness evaluation

Five composite discs of each material ( $\times 5$  manufacturers  $\times 2$  curing systems  $\times 2$  aging categories), 8 mm diameter  $\times 5$  mm thick, were embedded in epoxy resin (Bioplastic) so that a flat surface was exposed. The surface was serially polished through 600 grit silicon dioxide paper, followed by 6, 3, and 1  $\mu\text{m}$  diamond abrasives. A Knoop diamond on a Micromet microhardness tester (Buehler Ltd, Lake Bluff, IL, USA) was used under a 500 g load. For each sample, 6 indentations (6 indents  $\times 50$  samples  $\times 2$  aging categories) were performed prior to and after the aging treatment (total 600). The long diagonal of Knoop indentations were measured in the eye piece of the optical microscope on Micromet microhardness tester at  $50\times$ . In this study all materials were measured immediately after indentation. The Knoop hardness was calculated following the ISO 4545 [25] standard as well as VDI 1994 [26] as follows:

$$\text{KHN} = 1.451 \frac{F}{d^2} \quad (1)$$

Table 1  
Product parameters for the composites in this study

Curing mode	Product	Code	Manufacturer	Shade	Batch number	Recommended use	Filler weight in %	Filler size in $\mu\text{m}$
lc	Helioprogress	HP	Vivadent, Schaan, Liechtenstein	A2	B35974	Anterior	73.7 (16.2org)	0.01–0.1
cc	Isopast Variant	IV	Vivadent, Schaan, Liechtenstein	A2	Base: B36366, Cat: B18040	Anterior	39.4	0.02–0.05
lc	Polofil	PF	Voco, Cuxhaven, Germany	U	89500	Anterior	76	0.05, 10
cc	Alfacomp	A	Voco, Cuxhaven, Germany	U	Base: 98603, Cat: 98604	Anterior	69	<0.1, <30
lc	Pyramid Enamel	PD	Bisco, Schaumburg, IL, USA	A2	9900009794	Posterior	80	2
cc	Bisfil II	BF	Bisco, Schaumburg, IL, USA	U	Base: 9900009493, Cat: 9900007981	Posterior	80	<1
lc	Superlux Solar	SS	DMG, Hamburg, Germany	A2	98070684	Anterior	66 (25.0org)	0.05–2
cc	Superlux P/Anterior	SP	DMG, Hamburg, Germany	U	Base: 99230322, Cat: 99230322	Anterior	58 (25.0org)	0.05–2
lc	Vitalescence	VL	Ultradent, South Jordan, Ut, USA	A2	343 LOT 3KR3	Anterior/posterior	75	0.7
cc	Permalute	PL	Ultradent, South Jordan, Ut, USA	A2	REF/UP 695	Anterior/posterior	70	1.5

where  $F$  is the force in Newton (N) and  $d$  is the long diagonal of the Knoop indentation in mm.

## 2.2. Color evaluation

Discs were prepared with a diameter of 20 mm and a thickness of 1 mm, following the ISO 4049 specification [25]. A plastic split ring that rested on a glass slab was used to fabricate the samples. Three specimens for each composite (5 manufacturers  $\times$  2 curing systems) were made, for a total of 30. The chemically-cured materials were mixed following the manufacturers' instructions and syringed into the split ring and pressed between two pieces of glass. Chemically-cured specimens were allowed to cure for 60 min in a dark box before removing them from the split ring. Light-cured composites were applied to the split ring in between two glass slabs and cured according to the manufacturers' directions, using an Optilux light-curing unit (Demetron, Danbury, CT, USA). All specimens were finished with 320 grit paper to standardize the surface and stored for 1 week at 37 °C and 100% relative humidity prior to aging. Since a likely effect of aging is a change in surface texture, including increased roughness, a relatively rough surface finish was selected, to mask any changes due to aging. To determine the baseline color, specimens were measured with the UV/VIS/NIR Spectrophotometer Lambda 19 (Perkin Elmer, Norwalk, CT, USA) with a Reflectance Spectroscopy Accessory CSTM-RSA-PE-19 (Labsphere, N. Sutton, NY, USA). This instrument utilizes a double beam ratio integrating sphere reflectometer that collects specular and diffuse reflectance. The white standard SRS-99-010-7698-a (Perkin Elmer, Norwalk, CT, USA) was used to verify calibration of the instrument. All specimens were scanned from 400 to 700 nm, with a data interval of 1 nm, at a speed of 480 nm/min. Post-treatment UV/VIS/NIR spectra were then obtained with the same methods used for pre-treatment spectra. Pre- and post-treatment reflectance measurements were stored in digital form and utilized for CIE  $L^*a^*b^*$  values for a 2° standard observer and for illuminant D65. In 1976 the Commission Internationale de l'Eclairage developed a Uniform Color Space (UCS) system relating the color calculation to tristimulus values. It was used to show the color difference quantitatively. Movements in the white-black (value scale  $L$ ), red-green ( $a$ ), and yellow-blue ( $b$ ) color planes (chroma scales) were compiled by the Perkin Elmer color program (Perkin Elmer, Norwalk, CT, USA) and converted into  $L^*a^*b^*$  values, which were then recorded and analyzed. Changes in overall color ( $\Delta E^*$ ) were calculated as follows:

$$\Delta E^* = \sqrt{(\Delta L^*)^2 + (\Delta a^*)^2 + (\Delta b^*)^2} \quad (2)$$

## 2.3. Accelerated aging process

After examining samples at baseline, samples were artificially aged in a weathering machine (Ci35 Weather-Ometer,

Atlas Electronic Devices Co., Chicago, IL, USA) and exposed to a controlled-irradiance xenon arc filtered through borate borosilicate glass of 0.55 W/m<sup>2</sup>/nm measured at 340 nm. The test was run for a total radiant energy of 150 kJ/m<sup>2</sup> and a total exposure time of 122 h (80 h light on). The aging conditions [1,4] were as follows: test cycles: 40 min light only, 20 min light plus front water spray, 60 min light only, 60 min dark plus back water spray; dry bulb temperature: 47 °C (light) and 38 °C (dark); humidity: 50% (light) and 95% (dark); black panel temperature: 70 °C (light) and 38 °C (dark); and water temperature: 50 °C.

## 2.4. Statistical analysis

For statistical analysis of the hardness values, the mean of the six indentations per sample was used. The hardness data were analyzed by a three-way analysis of variance (ANOVA) with the factors of manufacturer (Vivadent, VOCO, Bisco, DMG, or Ultradent), curing system (light or chemically), and aging process (before or after) using the StatView software program (SAS Institute Inc., Cary, NC, USA). The Tukey–Kramer test was applied for pairwise comparisons; 95% confidence intervals were used throughout. Because of apparent statistical interactions, additional two-way ANOVAs were applied to the hardness data, comparing the aging versus curing methods for each of the five manufacturers. Paired  $t$ -tests were conducted for each manufacturer and curing system to assess changes in color ( $\Delta E^*$ ). Two-way ANOVA was conducted with the factors of manufacturer and curing system. In addition, one-way ANOVAs analyzed for light-cured materials versus manufacturers and chemically-cured materials and manufacturers. The change in color was evaluated as  $\Delta E^*(2)$  comparing pre- to post-treatment. For each of the ten composites (five manufacturers and two curing methods), the Pearson correlation coefficients ( $r$ ) of mean  $\Delta E^*$  values with the mean baseline hardness measurements and the mean percent change in hardness were computed. (Mean values were used since the samples that had hardness tested were not the same ones that had color changes tested) The correlation coefficient was also calculated to examine the relationship between mean baseline hardness of the composite with the filler fraction, using the weight percent.

## 3. Results

### 3.1. Mechanical properties

The polished surfaces of light-cured and chemically-cured samples before aging are shown in Fig. 1(a) and (b), while Fig. 1(c) and (d) show aged surfaces. The mean (standard deviation) percent hardness changes ranged from 4.8% (1.5%) for BF (cc) up to 32.1% (8.7%) for SS (lc) (Table 2).

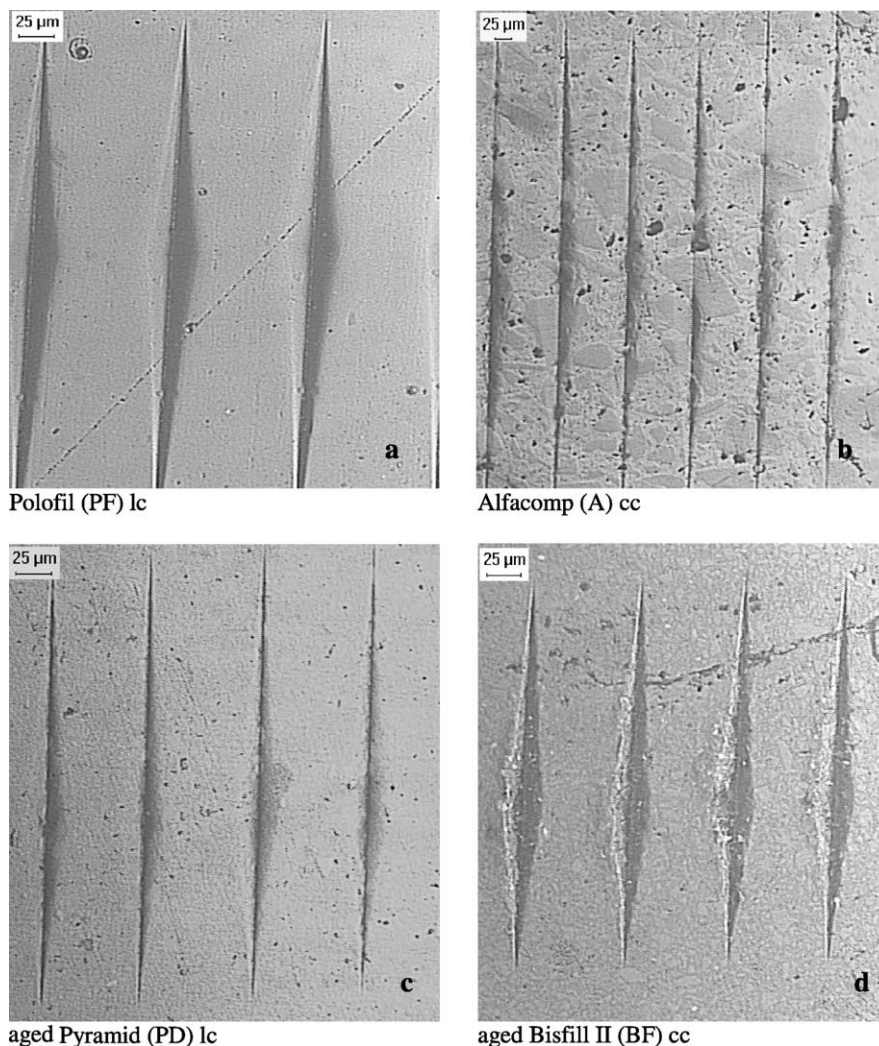


Fig. 1. Polished surface of (a) PF and (b) A with Knoop hardness indentation before aging process. Sharp edges of the indentation are visible in PF, a large quantity of macro filler was visible in A. Indentation after accelerated aging is represented in (c) PD and (d) BF, where PD and BF indicate no sharp edges. Samples are viewed in transmission light microscopy (original magnification a = 20×, b = 10×, c = 20×, d = 20×).

The three-way ANOVA showed significant differences among manufacturers, aging processes, and curing processes, as well as interactions among these groups. Considering the factors ‘manufacturers’ and ‘curing system’ a highly significant interaction of direction (the curing

Table 2  
Hardness and color changes of light cured and chemically cured composites, mean (SD)

Light cured composites	Hardness change in %	Color change ( $\Delta E^*$ )	Chemically cured composites	Hardness change in %	Color change ( $\Delta E^*$ )
HP	15.9 (3.6)	2.0 (0.4)	IV	18.2 (3.5)	11.2 (0.7)
PF	12.8 (5.3)	1.6 (0.9)	A	31.4 (5.4)	6.2 (0.6)
PD	14.1 (5.5)	5.3 (0.6)	BF	4.8 (1.5)	5.7 (0.6)
SS	32.1 (8.7)	2.2 (0.3)	SP	19.4 (2.9)	8.7 (0.7)
VL	15.1 (2.7)	5.8 (1.7)	PL	11.4 (1.9)	15.5 (0.8)

Table 3  
ANOVA table for three way ANOVA for hardness tests

	DF	Sum of squares	Mean square	F-value	P-value
Manufacturer	4	49571.733	12392.933	1727.515	<0.0001
Aging	1	1424.308	1424.308	198.542	<0.0001
Curing system	1	117.940	117.940	16.440	0.0001
turer*aging	4	65.305	16.326	2.276	0.0683
Manufacturer*-curing system	4	7510.321	1877.580	261.726	<0.0001
Aging*aging*-curing system	1	78.146	78.146	10.893	0.0014
Manufacturer*-aging*curing system	4	89.257	22.314	3.111	0.0197
Residual	80	573.908	7.174		

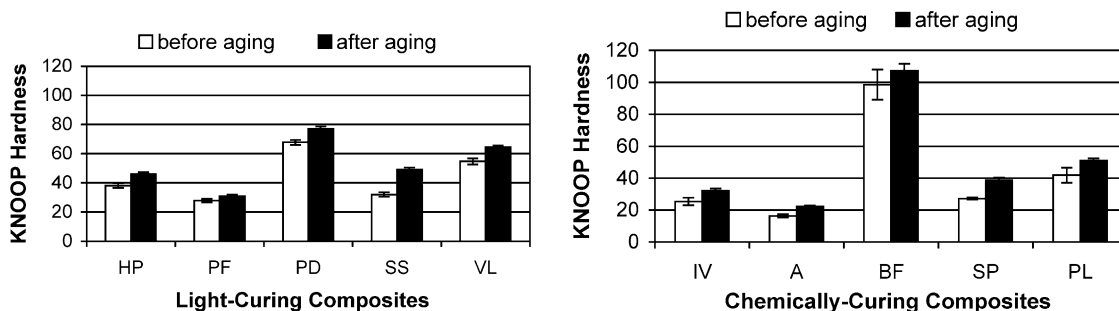


Fig. 2. Bar graph depicts mean Knoop hardness evaluation of light cured and chemically cured composites, before and after aging process due to circulating light and water exposure in Weather-Ometer machine. Standard deviations are indicated by vertical line on each bar.

system effect is reversed for one manufacturer) was found. The 3-way ANOVA results are shown in Table 3. Significant pairwise (two-way) interactions mean that the role of one factor depends on another. Three-way interactions mean that the two-way interactions do not completely describe the patterns. Typically, in the presence of interactions additional analyses are undertaken, for example, separately for each manufacturer, to make interpretation easier. Despite these interactions, certain consistent patterns are evident. The BF material had the highest degree of hardness prior to aging, as well as after aging, and is the only chemically-cured material with better properties than its light-cured counterpart. Knoop hardness mean (SD) for BF, prior and after aging treatment, were 98.6 (9.5) and 107.3 (4.4) KHN, respectively. Among the lcs for anterior applications, VL followed by HP, resulted in the highest hardness for this material group with 55.1 (2.6) and 39.4 (2.6) KHN prior to aging, respectively. This is the reason for the significant manufacturer  $\times$  curing system interaction, which was one of direction. The remaining interactions are of magnitude only, meaning that similar relationships are found, but that the strength of that relationship differs (Fig. 2, PD versus BF). Additional two-way ANOVAs were applied for each manufacturer to further discern the interaction among the curing and aging methods. Examining these factors more closely resulted in two material groups (Vivadent: HP, IV; DMG: SS, SP) where no interactions but significant differences were found, meaning the effect of

aging treatment was similar for each curing method. Each material showed a significant increase in hardness after the aging treatment and light-curing resulted in significantly harder samples than chemical-curing (Fig. 2). There were also significant differences among manufacturers except between Vivadent and DMG. No correlation could be found between the baseline hardness of the material and the filler content (wt%) of the composite,  $r = 0.20$ .

### 3.2. Color change

Means and standard deviations for values of  $\Delta E^*$  are shown in Fig. 3 for light-cured and chemically-cured materials. All 10 groups were significantly different than zero (Fig. 3), indicating significant color change. Statistically significant differences determined by two-way ANOVA were observed among manufacturers, between curing systems, and there was an interaction between manufacturer and curing system. The interaction was significant due to essentially no difference between the light- and chemically-cured  $\Delta E^*$  values for the Bisco products (BF and PD) in a one-way ANOVA. Additionally, one-way ANOVAs were conducted among the five manufacturers, separately for each curing process. Among the light-curing composites, the Ultradent and Bisco products were not significantly different from each other but the color changes were significantly higher than for Vivadent, VOCO and DMG. For the chemically-

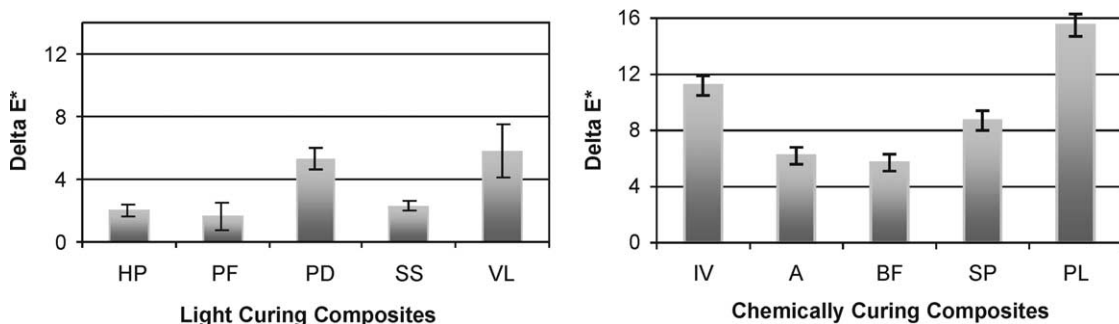


Fig. 3. Bar graph shows effect of mean total color change ( $\Delta E^*$ ) in light cured and chemically cured composites due to accelerated aging in Weather-Ometer machine for a total of 122 h with 80 h xenon arc exposure ( $150 \text{ kJ/m}^2$ ). Standard deviations are indicated by vertical line on each bar.

cured materials, only the Bisco and VOCO materials had  $\Delta E^*$  values that did not differ. Among all the other products significant differences exist, with the largest color change for PL.

The lc products HP, PF and SS had the least color change, with values in the range of 1.6–2.2 and were visibly perceptible. The Bisco products PD and BF II as well as VL from Ultradent were in the range of  $\Delta E^*$  5.3–5.8 and thus, showed very obvious differences. The remaining materials showed even greater color changes, which might be unacceptable in clinical situations.

A correlation coefficient comparing the  $\Delta E^*$  values with the baseline hardness data resulted in  $r = 0.01$ , showing no correlation between hardness and color change. Also, no correlation was found between color change ( $\Delta E^*$ ) and hardness percent change ( $r = 0.20$ ).

#### 4. Discussion

The materials in this study were mainly anterior composites, with the exception of the posterior composites from Bisco. The results of the mechanical properties clearly show higher hardness for the posterior composites, with BF (cc) 2–3 times higher than other cc's, probably due to its higher filler content (80 wt%). The lowest filler content (39.4 wt%), combined with the smallest filler size (0.02–0.05  $\mu\text{m}$ ), resulted in the lowest hardness for any material (IV, cc) used in this study. Among the lc's for anterior applications, VL, with 75.0 wt% filler content and an average filler size of 0.7  $\mu\text{m}$ , appeared to be the hardest material. This was followed by HP with 73.7% filler fraction and filler sizes from 0.01 to 0.1  $\mu\text{m}$ . There was a significant difference in hardness of VL and HP prior to aging, while the filler content was almost the same. This emphasizes that high hardness values are not related only to high filler content. The very modest correlation coefficient of 0.20 verifies these findings. The composition and the distribution of the filler sizes may be more important factors in hardness. The degree of conversion of the specimen was not measured in this study, but also has some impact on the hardness [23]. Chemically-cured materials often have lower degree of conversion than light-curing materials due to hand mixing and related disadvantages for the polymerization process. However, the hardness values of the cc composites are considerably less than those of the lc's. This also may be due to factors such as: more incorporation of more air bubbles; the cc's are not as homogenous due to hand mixing; and a thicker layer of oxygen inhibition on the surface [13,27].

A variety of mechanisms has been suggested for changes due to aging. Increased surface roughness after accelerated aging has been attributed to wear of the resin [1,28] or exposure of interior porosities [27,29]. Although hardness provides some evaluation of resistance of composites to compressive forces, variations in the microstructure, such as

large filler particles, may result in anomalously high hardness values. Inorganic filler (size  $>25 \mu\text{m}$ ) and air bubbles were visible (Fig. 1(b)) after indentation with the Knoop diamond in the A material (particle sizes  $<0.05$ ,  $<30 \mu\text{m}$ ) compared to the smooth surface of the lc PF (Fig. 1(a)) with 0.05 and 10  $\mu\text{m}$  as average particle sizes.

All the materials used in this study differ in particle sizes and filler amount (Table 1). Often several different resins are combined to enhance the properties. The proportions of the ingredients are proprietary, so that differences among the materials from different manufacturers are unspecified when comparing commercial products, as in this study. However, although proportions might vary, the components in the materials from all manufacturers were similar in lc and cc. To overcome the composition differences, experimental materials with a controlled composition would be appropriate.

The CIE  $L^*a^*b^*$  system uses the three parameters  $L^*$ ,  $a^*$  and  $b^*$  to define color [30]. The degree of lightness and darkness corresponds to  $L^*$ , while  $a^*$  and  $b^*$  are on the chromatic scale and represent red as  $+a^*$  and green as  $-a^*$ . Yellow corresponds to  $+b^*$  and blue to  $-b^*$ . Several authors have reported, that values of  $\Delta E^*$  in the range of 2–3 were just perceptible [4,6,29,31] and that  $\Delta E^*$  of 3.3 is the critical value for visual perception. On this basis, all of the composites in this study had perceptible color changes. Three composites (PF, HP, SS), all of them lcs, were rated as just perceptible, which may not be a clinically significant difference [3]. Two more lcs and one cc were ranked between 5.3 and 5.8, which may affect the decision for replacing the restoration and the remaining 4 cc materials would be esthetically unacceptable in clinical situations.

The results show significant differences between lcs and ccs and many factors contribute to this difference. The higher surface roughness causes more light scattering and loss of glossiness. Campbell et al. [32] reported a linear relationship between the optical scattering coefficient and the filler concentration. Chemical differences among the resin components, such as purity of the oligomers and monomers and concentration/type of activators, initiators, inhibitors, oxidation of unreacted carbon–carbon double bonds and fillers may affect the color stability as well. In the present experiment, the composites with the lowest filler contents had poor color stability, supporting the results of a previous study [10]. Furthermore, it should be mentioned that the specimens for color evaluation were finished to a 320 grit roughness, a relatively rough surface treatment which would not relate to a clinical situation. This condition was used to overcome the influence of increasing surface roughness after an aging treatment. Even though the surface roughness was not measured before and after the aging process, the surface structure did not appear to change perceptibly after the treatment and thus, probably did not have an important impact on the  $L^*a^*b^*$  determination, as predicted.

The specimens in this study were subjected to water and moderate temperature changes, while cycling in the Weather-Ometer machine. These moderate conditions were applied to avoid microcracking of the surface [28]. Thus the observed discoloration is probably related to water diffusion into the resin rather than microcracking. The low discoloration rate of BF in the cc group is therefore probably related to its high inorganic content and, provides this composite with a lower water sorption rate. To prove this assumption further investigations are necessary. In regard to discoloration, a previous study showed that initially improved surface properties may enhance resistance to water induced discoloration [5].

Chemically-curing composites often have been used in developing countries due to a lack of facilities, especially electricity, necessary to cure lc composites. Since chemically-cured materials tend to have worse color stability or low surface hardness than light-curing materials, new approaches are being sought. One new method is the development of blue LED-curing systems that have the ability to work with rechargeable batteries and might lead to promising results using light-curable composites for applications in developing regions.

## 5. Conclusions

The hypothesis that materials with high surface hardness correlate to less color changes after accelerated aging treatment was rejected. This study also demonstrated that each of the composites showed significantly increased hardness and perceptible color changes after accelerated aging. This verifies a part of the hypothesis. The light-curing materials were significantly more color stable than the chemically-curing anterior materials. Based on the results of this study, the chemically-cured composites evaluated have not yet reached the high demands of a long lasting esthetic anterior restoration.

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