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Effect of Bleaching on Color Change and Refractive Index of Dental Composite Resins

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This study investigated the effects of three bleaching agents (Whiteness Perfect, Whiteness Super, and Whiteness HP) on the color change and refractive index of three dental composites (Admira, Durafill VS, and Gradia Direct). Twenty disk-shaped specimens (10×2 mm) of each composite were prepared and divided into four subgroups (n=5). An unbleached group was used as a control, while the remaining specimens in the three subgroups were bleached with one of the bleaching agents respectively. Color change was assessed according to CIELAB color system and refractive indices were determined by phase modulated spectroscopic ellipsometry. Color differences between bleaching and baseline value (ΔE) were less than 3.3 for all groups. However, bleaching with Whiteness HP led to noticeable color changes for Admira and Durafill VS. While this agent had no effect on the refractive indices of these composites, the other two agents containing carbamide peroxide increased their refractive indices. Therefore, results suggested that replacement of such composite restorations may be required after bleaching.

Keywords: Bleaching, Composites, Color

INTRODUCTION

Bleaching is a relatively non-invasive approach to lightening teeth stained extrinsically or intrinsically. Bleaching techniques may be classified by whether they involve vital or non-vital teeth or whether the procedure is performed in-office or has an at-home component[1-3].

Bleaching agents usually contain some form of peroxide (generally carbamide and hydrogen peroxide) in gel or liquid form to be in contact with teeth for several minutes to several hours, depending on the formulation of material used[3-6]. It has been reported that bleaching effect is directly related to the exposure time and concentration of active bleaching ingredient[2,7]. The longer the exposure time and the higher the concentration of whitening material, the greater will be the oxidation process and color change. The associated side effects are namely porosity, increased surface roughness, and reduction in surface hardness of the existing composite restorations[2,8]. Previous investigations reported that the color change of resin composites was caused by many factors such as the chemical structure, chemical activator, resin initiator and inhibitor, activator process, polymer quality, type and quantity of filler, oxidation of unreacted C=C bonds, UV illumination, heat, and water[9,10].

Color assessments of teeth and composite materials after bleaching have been made using value-oriented shade guides, colorimeters, and digitized photographs — each with their own advantages and disadvantages[4,11]. The use of a colorimeter gives more objective results than shade tabs[4,7,11], but it is affected by some factors including translucency of the material tested[11].

Translucency is essential for dental restorative materials. Most of the organic molecules present in the matrix phase of dental composites and glasses (frequently used as fillers) do not effectively absorb visible light. As a result, scattering of light might be considered as the main reason for low translucency. Magnitude of light scattered depends on the dimensions and surface area of the dispersed phase (fillers), their segregation, microporosity, and surface roughness. These properties of the microstructure also affect the overall refractive index of the composite material. It should be noted that in general, magnitude and direction of scattering depends on the average magnitude of refractive index fluctuation in the composite material[12]. Therefore, individual refractive indices of the dispersed phase (fillers) and matrix phase (resin) should be perfectly matched in order to obtain transluceny close to that of tooth tissue[12,13]. If this were not so, the tooth would have poor esthetical properties and reduced cure depth with visible light[14]. In this respect, refractive indices are extensively used for the selection of composite materials.

Very often in daily dental practice, tooth-colored restorations exist in the teeth that are planned to be bleached[1]. Therefore, unintended application of the

bleaching products on existing restorations by the patients cannot be excluded if bleaching is not performed and monitored by the dentist[15]. The change of color and loss of shade match of composite restorations with surrounding tooth structure are perhaps the most frequent reasons for replacement of existing restorations after bleaching[6].

Many studies have evaluated the effect of bleaching agent on composite resin properties. One such investigation used a colorimeter to show that 10% carbamide peroxide gels somewhat lightened the color of composite resins[16]. In the same vein, analysis of surface reflectance showed significant changes in microfilled and hybrid resin composites after application of highly concentrated tooth whiteners with 30−35% hydrogen peroxide[17].

Due to significant advances in adhesive dentistry, resin composite materials have demonstrated ongoing improvements in strength, wear resistance, handling properties, and esthetics[3,12]. Besides, the introduction of ormocers has also brought on a range of highly esthetic composites. Ormocer is the term for organically modified ceramics. This class of material is characterized by incorporation of novel organic-inorganic copolymers in the formulation that allow a modification of the mechanical properties over a wide range[3]. Although some studies[7,18-20] have compared the effect of carbamide peroxide against hydrogen peroxide on resin composites ranging from microcomposite to polyacrylic resins, ormocers' bleaching-related changes in color have not yet been fully documented. It should be highlighted that drastic color changes in existing restorations may compromise esthetics. Therefore, it is also important to understand the effect of bleaching agents on the color of ormocer-based restorative materials.

This study was conducted to compare color changes and also refractive indices of a microfill, a microhybrid, and an ormocer-based resin composite exposed to bleaching agents of different formulation and concentrations.

MATERIALS AND METHODS

Composites

To examine the effects of three bleaching agents on the color change of resin composites, one product from each type of contemporary resin-based filling material was chosen to investigate if the composition

Table 1 Restorative materials used

	Admira	Durafill VS	Gradia Direct
Manufacturer	Voco, Cuxhaven, Germany	Heraeus Kulzer, Wehrheim, Germany	GC Corpo., Tokyo, Japan
Type	ormocer-based resin composite	microfill resin composite	microhybrid resin composite
Organic Martrix	anorganic-organic copolymers (ormocers), aliphatic and aromatic dimethacrylates	bisphenol-A dimethacrylate, urethane dimethacrylate	urethane dimethacrylate
Filler type	Ba-Al-B-silicate glass, SiO_2	pyrogenic SiO_2, splinter polymer	Fluoro-alumino silicate glass, silica and pre-polymerized fillers
Average particle size	0.04-1.2 μm (mean 0.7 μm)	pyrogenic SiO_2: 20-70 nm splinter polymer: 10-20 μm	0.85 μm
Filler volume %	56	40	64-65

Data are according to manufacturers' infomation.

Table 2 Bleaching agents used

	Whiteness Perfect	Whiteness Super	Whiteness HP
Composition	16% carbamide peroxide, glycol, distilled water, potassium nitrate, sodium fluoride	37% carbamide peroxide, neutralized carbopol, potassium ions, glycerin, deionized water	35% hydrogen peroxide, mixture of pigments, glicol, thickener, deionized water
Regime	daily application (3-4 hours) for 14 days	3 application (20 minutes each) with a 7 day interval	2 application (15 minutes each) with a 7 day interval

influenced the results. For all the chosen resin composites, shade A3 was used. Table 1 lists the composite materials and their details. Included were a microfill resin composite, Durafil VS; a microhybrid composite, Gradia Direct; and a ormoser-based composite, Admira.

Bleaching agents

The bleaching agents used were Whiteness Perfect (16% carbamide peroxide), Whiteness Super (37% carbamide peroxide), and Whiteness HP (35% hydrogen peroxide) (Table 2). All the selected bleaching agents were marketed by the same manufacturer (FGM Produtos Odontológicos, Joinville, SC, Brasil) for different applications and claimed not to bleach restorative materials. Whiteness Perfect was to be applied daily at home by the patients for 3−4 hours per day for 14 days consecutively. As for the other two products, they were recommended for in-office use by dentists for non-vital and vital teeth. It was recommended that Whiteness HP be applied for 15 minutes each for two sessions, whereas Whiteness Super for 20 minutes each for three sessions.

Specimen preparation

Twenty disk-shaped specimens from each resin composite material (60 specimens in total), 10 mm in diameter and 2mm in depth, were prepared in Teflon molds. The materials were handled according to manufacturers' instructions. The mold was placed on a transparent polyester film strip (3M Flip-Frame, 3M Visual Systems Division, Austin, TX, USA) and a glass microscope slide. The composite was packed into the mold until it was intentionally overfilled. The material was covered with another polyester film strip and a glass microscope slide. Excess material was extruded by light pressure, and resin composites were polymerized using a blue light-emitting diode (LED) unit (UltraLight PB-070, Fine Vision Electronics Co., Sanchung City, Taipei County, Taiwan). This source emitted light at 440−480 nm, and had an intensity of 1000 mW/cm^2. Curing time was set at 20 seconds. Distance between the light source and specimen was standardized by the use of a 1-mm glass slide. The end of the light guide was in contact with the cover glass during polymerization. After light curing, all specimens were stored in distilled water for 24 hours at 37℃ to ensure complete polymerization. The top surfaces of the specimens were then polished flat using a sequence of 600-, 800-, and 1200-grit silicon carbide papers and Sof-Lex (3M ESPE, USA) disks.

Bleaching procedure

Twenty specimens from each composite group were randomly divided into four subgroups. For control, five specimens of each composite were immersed in distilled water. Then, five specimens in each subgroup were bleached by one of the bleaching agents. To simulate the bleaching process, the first subgroup was immersed in Whiteness Perfect (16% carbamide peroxide gel) for three hours for 14 consecutive days; the second subgroup immersed in Whiteness Super (37% carbamide peroxide gel) for 20 minutes for three sessions; the third subgroup immersed in Whiteness HP (35% hydrogen peroxide gel) for 15 minutes for two sessions. Whiteness Super and Whiteness HP were applied in intervals of seven days. Throughout the experiment, specimens were stored in a dark environment at room temperature (23±1℃). During test intervals, the specimens were rinsed with tap water for one minute to remove the bleaching agents, blotted dry, and placed in Petri dishes filled with distilled water for storage. For each new session, bleaching agents were replenished accordingly.

Color assessment

Before and after treatment with each of the bleaching agents, the surface of each specimen was inspected to determine whether any changes in the color of the specimen's surface were visible to the naked eye. Before baseline color measurement, specimens were rinsed under tap water for one minute and blotted dry. A colorimeter (Mercury™ 2000, Datacolor, Lawrenceville, NJ, USA) was used to record the color variables according to the CIELAB (Commission Internationale de l'Eclairage L*, a*, b*) system.

Aperture size diameter was 5 mm and illuminating and viewing configurations were CIE diffuse/8° . The illumination source was provided by a pulsed xenon lamp filtered to D65, and a white calibration ceramic was used (CIE L* = 95.93, a* = −0.41, and b* = 1.56). The specimens were positioned so that their surfaces were in contact with the aperture head of the colorimeter. Each specimen was measured twice by the same person, and the average baseline values of L*, a*, and b* were calculated. L* represents the degree of gray and corresponds to a value of brightness, such that high L* values are obtained from bright or white specimens. The value a* represents the red-green axis, and the value b* represents the blue-yellow axis.

After bleaching, the same procedure was repeated to determine the chromatical values. Magnitude of total color difference (ΔE^*) was calculated using the following equation[21]:

$$\Delta E^* = [(\Delta L^*)^2 + (\Delta a^*)^2 + (\Delta b^*)^2]^{1/2}$$

where ΔL^*, Δa^*, and Δb^* are changes in L*, a*, and b* after bleaching, respectively. ΔE^* values >1 were considered to be visible to the naked eye, and $\Delta E^* \geq 3.3$ was considered as clinically unacceptable[9].

Determination of refractive index

Refractive indices of specimens were determined by phase modulated spectroscopic ellipsometry at a 70° angle of incidence (HORIBA UVISEL, Jobin Ivon, Chilly Mazarin, France). The measurements were performed in configuration II where the modulator and analyzer angles were fixed to 0° and 45° respectively. All measurements were performed with a spot size of 2.9 mm². The ratio of complex reflection coefficients of an incident light polarized parallel (r_p) and perpendicular (r_s) to the plane of incidence was expressed in terms of ellipsometric angles Ψ and Δ as $\rho = \frac{r_p}{r_s} = \tan(\Psi)e^{i\Delta}$. The refractive index n of specimen was determined by assuming a simple air/material (one interface) model and that the material was assumed as nonabsorbing[22]. Within the frame of this method, refractive index was determined using the following equation[23]:

$$n = \sqrt{\sin^2\phi_0\left[1+\tan^2\phi_0\left(\frac{1-\tan\Psi e^{i\Delta}}{1+\tan\Psi e^{i\Delta}}\right)^2\right]}$$

where ϕ_0 is the angle of incidence and $i=\sqrt{-1}$. The angles Ψ and Δ determine the changes in amplitude and phase, respectively, of the p (parallel) and s (perpendicular) components of a wave upon reflection. ρ is equivalent to the ratio of the polarization states of reflected and incident waves.

Scanning microscope analysis

For the evaluation of topography and surface structure, a total of 12 specimens were examined. One specimen from each bleaching agent and one control specimen was selected for each resin composite. After sputter-coating with 25 to 30 μm of gold (Hummer VII, Analect, USA), the specimens were examined at ×2000 magnification with a scanning electron microscope (SEM) (Jeol JSM 6400, Noran Instruments, Tokyo, Japan).

Statistical analysis

After data collection, mean values and standard deviations were calculated by using a SPSS statistical software program (version 13.0, SPSS Inc., Chicago, USA). The data were subjected to statistical analysis using two-way analysis of variance (ANOVA). Where significant differences were present, Tukey's *post hoc* test was applied to make pairwise comparison at a significant level of 0.05.

RESULTS

Table 3 and Figs. 1a−c show the chromatical values of resin composites before and after bleaching. For the L* values, it could be seen that Admira and Durafill VS — not Gradia Direct — showed increase in brightness with the different bleaching agents. For the a* values, all the bleached specimens of Admira showed small shifts when compared to the control. By contrast, Durafill VS and Gradia Direct resin composite specimens bleached with Whiteness Perfect (16% carbamide peroxide) revealed a relatively larger shift in a* value when compared to the controls and their other own bleached specimens. For the b* values, all resin composites tended to shown an increase with the use of Whiteness HP (35% hydrogen peroxide). This led to a yellow shade of the specimens that was visible to the naked eye.

A complete evaluation of color changes based on ΔE* values by two-way ANOVA revealed an interaction between the bleaching agents and resin composites ($F=141.229$). The highest score was recorded for Admira bleached with Whiteness HP, while microhybrid resin composite Gradia Direct bleached with Whiteness Super (37% carbamide peroxide) ranked the lowest among the materials (Table 4, Fig. 1(d)).

To clarify the effect of different bleaching agents on the same resin composite, Tukey's test revealed that the color of each composite did not change statistically when bleached with Whiteness Perfect and Whiteness Super ($p>0.05$). However, when compared against Whiteness HP for Admira and Durafill VS specimens, the use of the former two bleaching agents registered statistically significant differences ($p<0.05$) respectively. For Gradia Direct specimens bleached with Whiteness Super and Whiteness HP, the color change was found to be significant when comparing the mean ΔE* values of the specimens ($p<0.05$). Conversely, for Gradia Direct specimens bleached with Whiteness Perfect and Whiteness HP, no statistically significant differences were noted ($p>0.05$).

Bleaching with 16% and 37% of carbamide peroxides led to statististically significant differences among the resin composites ($p<0.05$). Color change was found to be statistically significant for all the resin composites except for Admira and Durafill VS. On the other hand, the color changes of the three resin composites tested were found to be statistically different from each other after bleaching with 35% hydrogen peroxide ($p<0.05$).

Figure 2 shows the refractive indices of the composites before and after bleaching. The refractive indices of unbleached specimens of Admira and Durafill VS resin composites were found to be higher than those of Gradia Direct (1.425, 1.425, and 1.375 respectively). The refractive indices of Admira and Durafill VS resin composites increased as they were bleached with both carbamide peroxide gels, being more so with 37% carbamide peroxide. As for Gradia Direct, bleaching with both carbamide per-

Table 3 ANOVA analysis results of the chromatical values of L*, a*, and b*

Resin composite	Groups	L*	a*	b*
Admira	Control	72.95±0.18	0.65±0.02	3.55±0.02
	WP	73.64±0.12	0.59±0.01	3.61±0.02
	WS	73.68±0.12	0.76±0.02	3.63±0.10
	WHP	74.28±0.13	0.65±0.02	4.02±0.02
Durafill VS	Control	75.44±0.20	0.14±0.05	3.52±0.22
	WP	75.78±0.15	0.70±0.02	3.69±0.02
	WS	76.20±0.06	0.30±0.02	3.74±0.07
	WHP	76.14±0.05	0.23±0.02	4.38±0.02
Gradia Direct	Control	74.30±0.15	0.92±0.07	4.64±0.24
	WP	74.35±0.03	1.40±0.02	4.52±0.01
	WS	74.67±0.03	1.05±0.01	4.70±0.02
	WHP	74.51±0.02	1.06±0.01	5.17±0.02

n=5 specimens per experimental condition
Groups depicted as WP, WS and WHP are the speciments bleached with Whiteness Perfect, Whiteness Super, and Whiteness HP, respectively.

Table 4 Color changes (Δ E*) of restorative materials after bleaching

	Admira	Durafill VS	Gradia Direct
Bleaching Agents	Mean ± SD	Mean ± SD	Mean ± SD
Whiteness Perfect	$0.6956 \pm 0.1250^{a,A}$	$0.6893 \pm 0.0794^{c,B}$	$0.4962 \pm 0.0168^{A,B}$
Whiteness Super	$0.7496 \pm 0.1255^{b,C}$	$0.8073 \pm 0.0606^{d,D}$	$0.4007 \pm 0.0288^{e,C,D}$
Whiteness HP	$1.4117 \pm 0.1180^{a,b,E,F}$	$1.1133 \pm 0.0290^{e,d,F,G}$	$0.5874 \pm 0.1400^{e,E,G}$

n=5 specimens per experimental condition
By two-way ANOVA: F=141.229, p=0.000, p<0.05.
Tukey's test indicates statisticl difference (p<0.05) for means followed by the same letters; small letters in the column are for the comparison of different bleaching agents within the same material; capital letters in the rows are for the comparison of the composites bleached with the same agent.

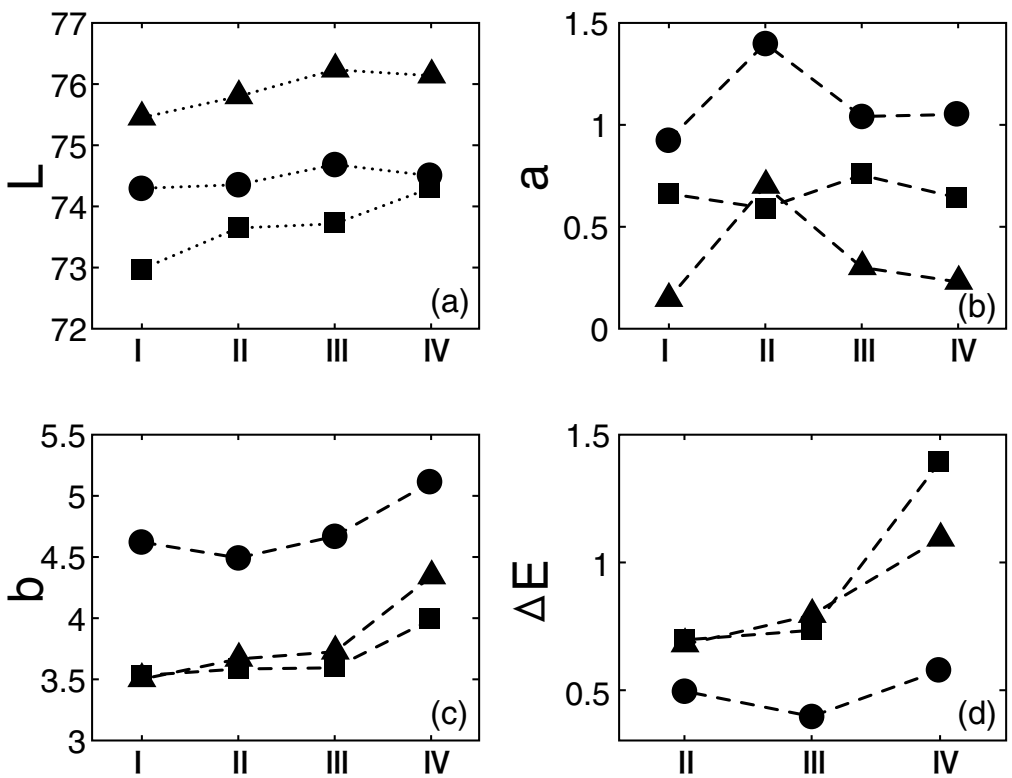

Fig. 1 Chromatical values (a) L*, (b) a*, (c) b* and (d) Δ E* of the specimens. I, II, III, and IV show unbleached and bleached specimens with Whiteness Perfect, Whiteness Super, and Whiteness HP respectively. Resin composites Admira, Durafill VS, and Gradia Direct are denoted by squares, triangles, and circles respectively. Magnitude of standard deviation is within the marker size.

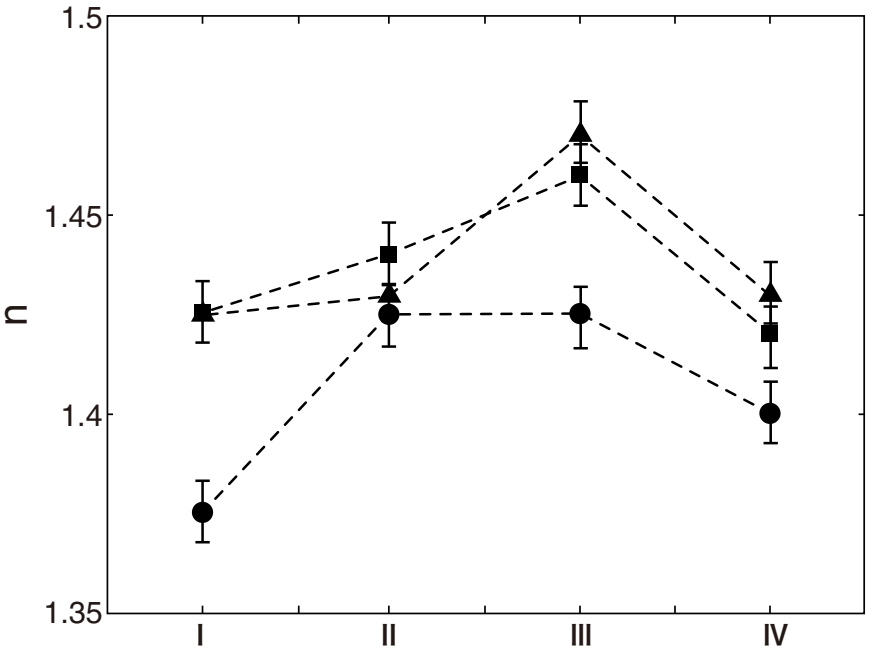

Fig. 2 Refractive indices of specimens at a wavelength of 632.8 nm for samples (I) unbleached and bleached with (II) Whiteness Perfect, (III) Whiteness Super, and (IV) Whiteness HP agents. Resin composites Admira, Durafill VS, and Gradia Direct are denoted by squares, triangles, and circles respectively.

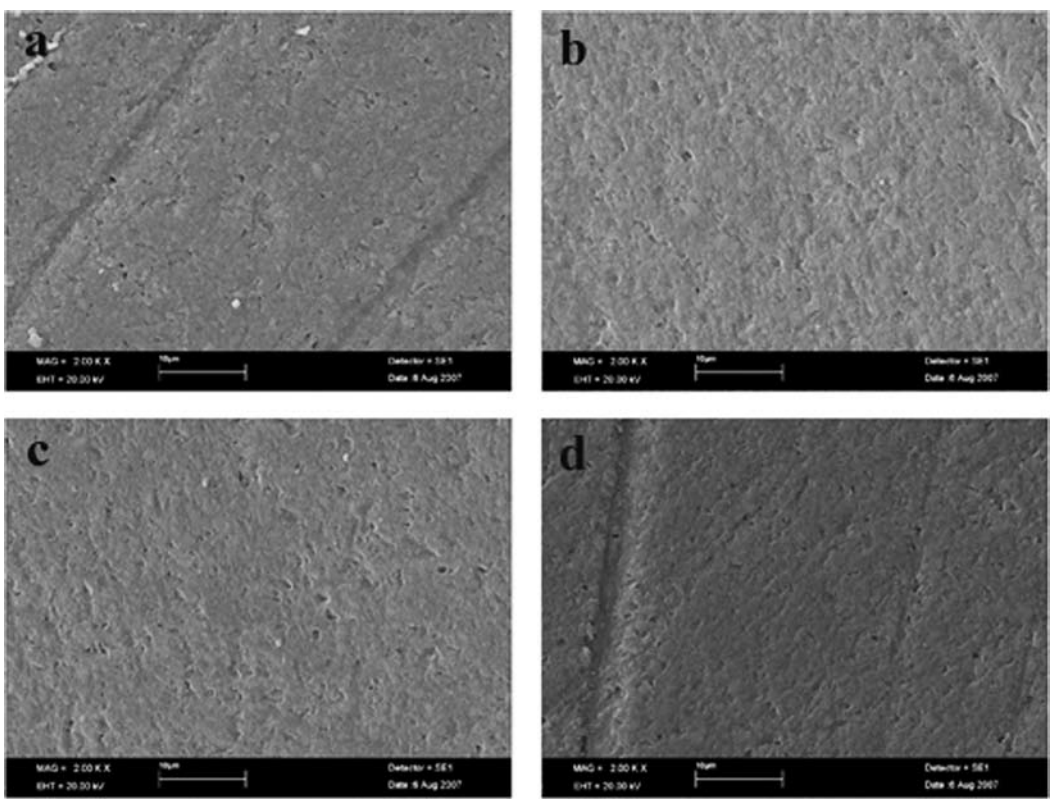

Fig. 3 Representative SEM images of Admira: (a) control group; (b) Whiteness Perfect group; (c) Whiteness Super group; and (d) Whiteness HP group (original magnification ×2000).

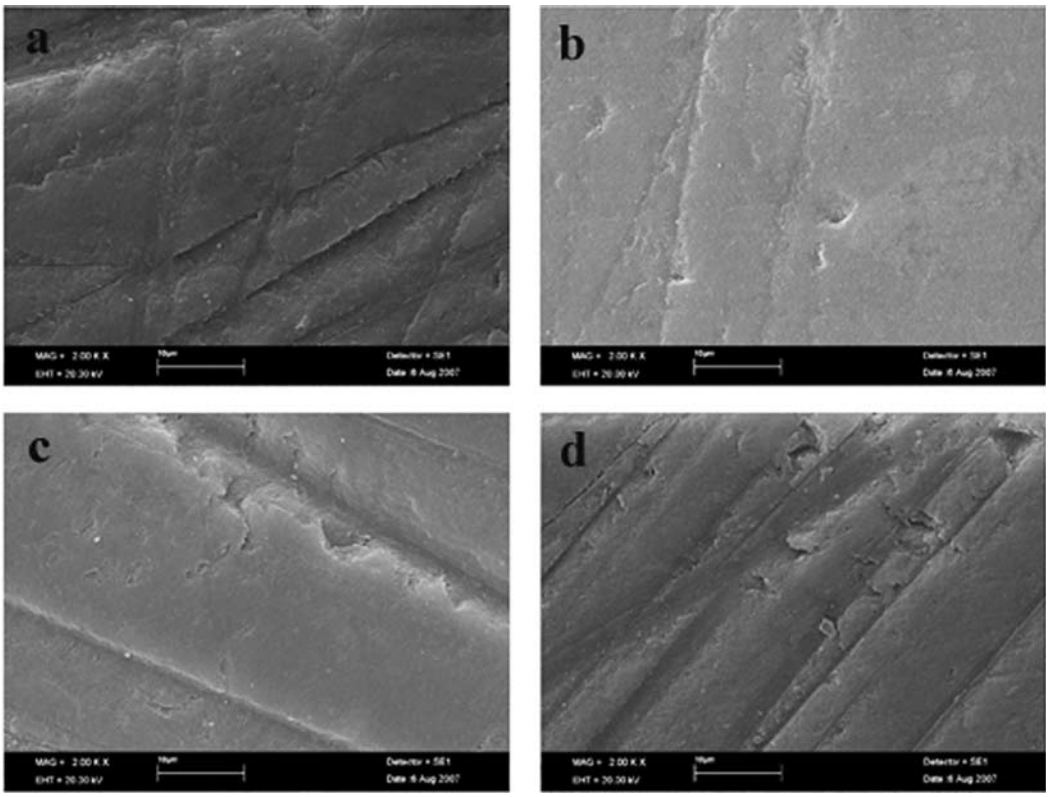

Fig. 4 Representative SEM images of Durafill VS: (a) control group; (b) Whiteness Perfect group; (c) Whiteness Super group; and (d) Whiteness HP group (original magnification ×2000).

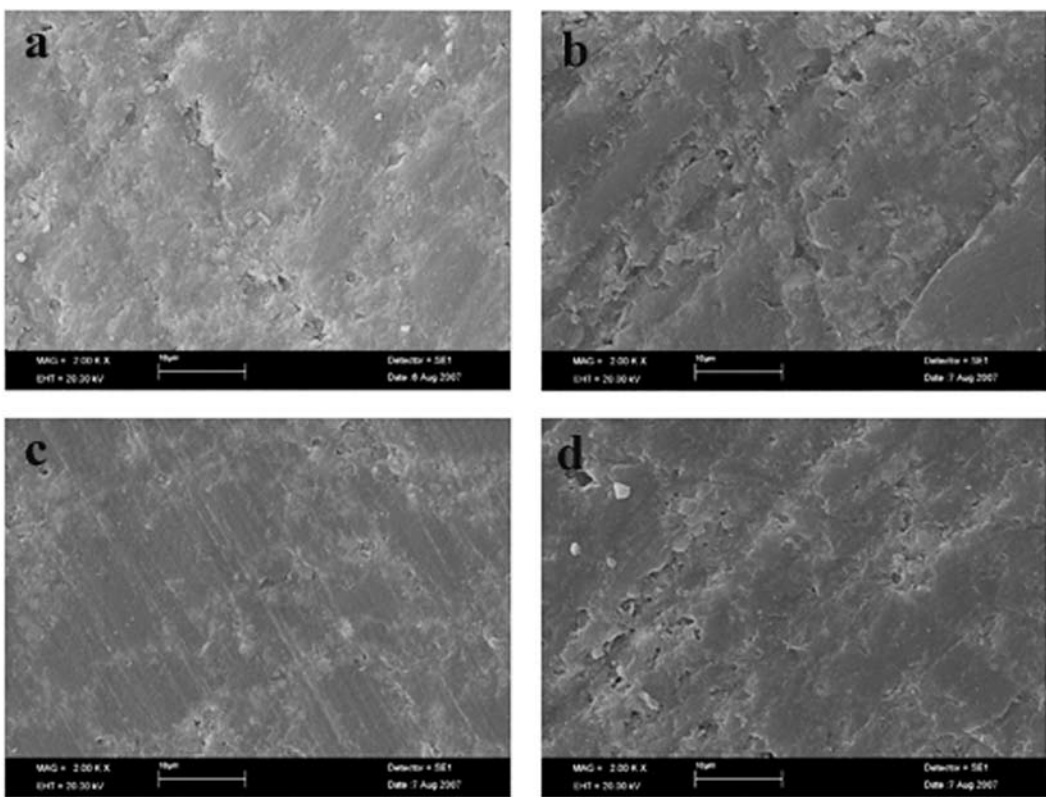

Fig. 5 Representative SEM images of Gradia Direct: (a) control group; (b) Whiteness Perfect group; (c) Whiteness Super group; and (d) Whiteness HP group (original magnification ×2000).

oxide gels led to increased refractive indices — but the differing concentrations of carbamide peroxide did not result in significant differences between the two refractive indices. Bleaching with 35% hydrogen peroxide did not affect the refractive indices of Durafill VS and Admira; however, a considerable change was observed for Gradia Direct resin composite.

Figures 3−5 show the typical SEM images of the resin composites. In each figure were included the surfaces of the composite for unbleached (*i.e.*, control) (a) and bleached with Whiteness Perfect (b), Whiteness Super (c), and Whiteness HP (d). The surfaces of all the control specimens were seen as relatively flat. However, those of Admira and Durafill VS presented an irregular area with some indentations which might be a result of the polishing procedures (Figs. 3a, 4a, and 5a). After bleaching, all the Admira samples showed shallow pitting on the whole surface (Figs. 3b−d). Additionally, a river-like pattern was seen on the surface bleached with Whiteness HP (Fig. 3d). For Durafill VS samples, there were also some observable effects of bleaching agents on the surface morphology. Whiteness Perfect led to etching-like features such as striations and larger pitting on the surface (Fig. 4b), whereas the sample bleached with Whiteness Super showed evidence of some deeper-splitting features such as river-like patterns (Fig. 4c). The latter appearance was also seen on the surface bleached with Whiteness HP, but to a worse extent (Fig. 4d). Nonetheless, apart from the aforementioned specific features, the remaining surfaces of all Admira and Durafill VS samples were observed to be relatively smooth. For Gradia Direct, the sample bleached with Whiteness Super did not seem to be much affected in surface morphology, when compared to bleaching by the other two agents. The sample bleached with Whiteness Super seemed to be relatively flat (Fig. 5c), whereas the other two samples exhibited more irregular features — such as small pores and scratches — and a rougher surface (Figs. 5b and d).

DISCUSSION

Tooth bleaching has become extremely popular. Owing to its widespread popularity, the effect of this procedure on the esthetic appearance of resin composites — which may exist in teeth — needs to be taken into consideration. In particular, the organic matrices of resin composites are prone to chemical alteration induced by the acidic component of bleaching agents. This may then compromise the color matching of resin composite restorations to adjacent tooth structure, giving a reason for their replacement[15,24].

In color assessment, the choice of an appropriate method is important because of the path length of incident light in the material tested[21]. It is well known that instrumental evaluation presents more objective data *versus* the subjectivity of visual color determination[4,7,10,11]. On this ground, a colorimeter with white colored plate for the background was used in the present study. The chromatical values backed by a white colored plate could be considered as the color of resin composites applied on the lining material in the oral cavity[10].

It has been reported that two key factors determine the overall whitening efficacy of peroxide-containing products: peroxide concentration and application duration[4]. Therefore, to determine the changes in color and refractive indices of three resin composites subsequent to bleaching, 16% and 37% carbamide peroxide and 35% hydrogen peroxide were tested as bleaching agents using different application times (Tables 1 and 2).

Upon examining the chromatical values of the bleached resin composites, it could be seen that ormocer-based and microfill resin composites showed somewhat an increase in brightness — based on L* values — after bleaching with the different agents. For the a* values, small shifts were observed for all the bleached specimens of ormocer-based composite, whereas relatively large shifts were observed for microhybrid and microfill resin composite specimens after bleaching with 16% carbamide peroxide. Although it is difficult to give a clear explanation for this phenomenon, some amine synergists may create red/brown by-products to a certain extent[9]. For the b* values, a heightened increase was observed for all the tested composites following the use of 35% hydrogen peroxide. This led to a yellow shade which was noticeable to the naked eye.

Several authors have shown that color differences greater than 1 ΔE^* unit were considered to be visible to the naked eye by 50% of human observers, and ΔE^* values equal to or greater than 3.3 were considered as clinically unacceptable[25-27]. In the present study, none of the bleaching regimes resulted in color changes with $\Delta E^* \geq 3.3$. However, application of 35% hydrogen peroxide gave $\Delta E^* > 1$ for ormocer-based and microfill resin composites. The interaction between this bleaching agent and restoratives could be of clinical significance, as the color change could be noticeable to the patient. On the other hand, the use of 16% and 37% carbamide peroxide did not lead to noticeable color change of the restoratives used because the amount of color change of the bleached specimens were lower than 1 ΔE^* unit.

Differences in the bleaching effect of the agents on the same material might be attributed to their different hydrogen peroxide contents. The higher efficacy of 35% hydrogen peroxide gel could be due to an excess of active ingredient that readily diffused. It is

noteworthy that carbamide peroxide is a vehicle for the delivery of low concentrations of hydrogen peroxide[5]. During the process, one-third of carbamide peroxide decomposes into hydrogen peroxide and the rest into urea[2,4,5,7]. Urea further breaks down into ammonia and carbon dioxide, thereby enabling the evaluation of intraoral pH[3].

Hydrogen peroxide is an aggressive oxidant capable of degrading the polymer matrix of resin-rich composite materials[3,15,28]. It breaks down into water and oxygen, as well as free radicals which result in oxidation of the pigments or amine compounds within the structure[2,3,20]. In addition to its reactivity, hydrogen peroxide demonstrates an extensive ability for diffusion[15]. Oxidation of the pigments may occur as a result of direct interaction with hydrogen peroxide on the resin surface[21]. Peroxides might induce oxidative cleavage of polymer chains. Therefore, any unreacted double bonds are expected to be the most vulnerable parts of the polymers. Furthermore, free radicals induced by peroxides may impact the resin-filler interface and cause filler-matrix debonding. Microscopic cracks are formed, resulting in surface roughness and leading to diffusion of agent[15].

In the present study, the resin composites used were tightly cross-linked with high-molecular-weight polymer molecules[21]. This could be a reason why there was not much color change. This finding was in good agreement with that of a previous study, whereby 10% carbamide peroxide somewhat lightened the color of composite resins[16]. Furthermore, in another study, color changes following the use of 10% carbamide peroxide for 312 hours were undetectable to the naked eye[20].

Due to their organic matrix, composite resin materials are rendered more prone to chemical alterations compared to inert metal or ceramic restorations[15]. Our results indicated that color change induced by the same bleaching agent might be dependent upon the monomer structure, volume of the resin matrix, as well as the filler systems of composite materials tested. The structures of the organic matrices of all the resin composites used in this study were different. The organic matrix of microfill composite contained bisphenol-A dimethacrylate and urethane dimethacrylate, whereas that of the microhybrid composite was based on urethane dimethacrylate only, hence it had lower surface hardness than the other composites tested. On the other hand, ormocer was based on a resin system in which multifunctional urethane- and thioether(meth)acrylate alkoxysilanes as sol-gel precursors have been developed for the synthesis of inorganic-organic copolymer ormocer composites as dental restorative materials. The alkoxysilyl groups of silane allow the formation of an inorganic Si-O-Si network by hydrolysis and polycondensation reactions, and the (meth)acrylate groups are available for photochemically induced organic polymerization. The ormocer matrix has been suggested to exhibit significantly less wear than composite matrices[29] and to have high surface hardness values because of a more rigid matrix[3]. However, in the current study, this material and microfill resin composite underwent a significant color change when bleached by an agent containing a high concentration of hydrogen peroxide. This suggested that the volume of resin matrix and filler type had a great influence on the color parameters of dental composites than the structure of the organic matrix[3,29].

It could be seen in Table 1 that the volumes of the resin matrices of ormocer and microfill composites were greater than that of microhybrid composite because of lower volumetric filler content. This meant that a higher degree of oxidation was induced by the bleaching agents in their resin polymer matrices[3]. Hydrogen peroxide is an aggressive oxidant capable of degrading the organic matrix and in turn breaks down into free radicals, which eventually combine to form molecular oxygen and water. Some aspect of this chemical process may accelerate the hydrolytic degradation of resin composites, leading to color change[28].

It has been suggested that barium-containing glass fillers are more susceptible to water attacks than both quartz and fairly purified amorphous SiO_2. However, because of a larger total surface area, the microfill particles have more Si available for leaking. The attack of water on the fillers might also influence the esthetic properties of the composites[30]. In this study, the materials tested contained different type of fillers (Table 1): ormocer had Ba-containing glass fillers and microfill resin composite contained pyrogenic SiO_2, which were likely to be softer than that of microhybrid composite including fluoroalumina silicate glass. Differences in the structures of the fillers could explain why the ormocer and microfill resin composites revealed greater color change compared to microhybrid composite after bleaching with a high concentration of hydrogen peroxide.

For dental materials, the overall refractive index (*i.e.*, pertaining to both resin matrix and filler particles) is generally larger than about 1.45[12,13,31,32]. Therefore, the resulting refractive indices of the composite materials seem somewhat underestimated[31]. The approach applied for the determination of refractive indices in this study assumed a simple air/material model which ignored the surface overlayer of the composite material. This surface overlayer might have come into existence due to surface roughness, surface reconstruction, surface oxide, etc. At this juncture, it must be reiterated that ellipsometry is a highly surface-sensitive measurement technique. The surface overlayer, which is not modelled in the

ellipsometric analysis, might result in a decreased density of the microstructure, which in turn leads to a smaller refractive index[33]. According to the Clausius-Mossotti relationship[34], the dielectric function is proportional to the density of polarizable species. Therefore, a decrease in the density of the microstructure would cause a decrease in the refractive index. It should also be noted that this eventual density deficit is not only restricted to the surface, but also translated to the bulk of the composite material. Within the frame of this approach, the obtained refractive index value should be referred to as an apparent or pseudo-refractive index value.

Debonding caused by water will result in gaps between the resin and fillers, changing the refractive index of the composite[30]. It has been shown that upon exposure to plaque acids, resin-based materials underwent softening and loss of surface integrity[35]. Similarly, although it was not studied in this study, the deletorius effect of oxidizing agents might impair the surface integrity, affecting the penetration depth of bleaching agent. This was a logical suggestion to propose because SEM images revealed that all the composites tested underwent surface alterations after bleaching (Figs. 3－5).

The refractive indices of the composites are given in Fig. 2. The refractive indices of unbleached ormocer, microfill, and microhybrid composites were determined as 1.425, 1.425, and 1.375 respectively. The surface of the microhybrid resin composite revealed more irregular features and seemed rougher (Fig. 5). It could thus be said that a decrease in the density of its microstructure contributed to the low refractive index of this composite. In addition, there was a stronger change in the surface morphology of this microhybrid composite bleached with 16% carbamide peroxide in comparison to ormocer and microfill composites. This observation was also echoed in the refractive index values shown in Fig. 2. In light of these observations, it was confirmed that the surface properties of a material considerably affected its overall apparent refractive index.

Upon bleaching with carbamide peroxide gels, the refractive indices of the resin composites exhibited an increasing tendency (Fig. 2). Bleaching with 35% hydrogen peroxide did not seem to affect the refractive indices of ormocer and microfill composites, whereas a considerable change was observed for microhybrid composite. In addition, the concentration of carbamide peroxide did not affect the refractive index of microhybrid resin composite — a behavior seemingly in agreement with the behaviors of b* and ΔE^* variables in Fig. 1.

The refractive indices of ormocer and microfill resin composite were found to be higher than those of microhybrid composite. The average particle size of the fillers in microhybrid was relatively larger than those of the other two materials tested, and such a large particle size might enhance microporosity in the structure. In this connection, it came as little surprise that smaller refractive index values were found for this microhybrid composite tested. On the other hand, this density deficit might only be partially related to the enhanced surface roughness, which promotes plaque accumulation[36].

With smaller filler particles, the specific surface area of the particles increases and consequently the interaction between the matrix and filler increases[14]. However, it should be noted that small particles may agglomerate in the matrix, thereby decreasing the interaction between the matrix and filler. The microfill composite has been found to show large aggregates made of silica microfillers, embedded in a prepolymerized organic matrix[32]. It had fine particles (pyrogenic SiO_2) which were much smaller than the large particles of splinter polymers[37]. According to the manufacturer's information, the ormocer used consisted of large prepolymerized molecules organized in a matrix of inorganic-organic copolymers, and that its surface-modified inorganic fillers were of spherical shape. Although the average particle size and filler shape of ormocer and microfill composites were quite different, their refractive index behaviors under different bleaching agents were similar. This observation suggested agglomerated fillers in the microfill composite. The similar strong changes in ΔE^* for these two materials also supported this suggestion. Further, the changes in chromatical values of ormocer and microfill specimens under different bleaching agents in Fig. 1 were very similar to the refractive index changes given in Fig. 2. At this juncture, it is noteworthy that color changes (*i.e.*, ΔE^*) of these materials with larger refractive indices were found to be stronger.

Based on the results obtained in this study, it could be concluded that the high concentration of hydrogen peroxide in a proprietary bleaching gel had a noticeable color change effect on ormocer-based and microfill resin composite restorative materials. Therefore, patients should be informed that replacement of such existing composite restorations may be required after tooth bleaching.

CONCLUSIONS

Within the limitations of this *in vitro* study, the following conclusions were drawn:

(1) None of the bleaching agents tested made any significant clinical effects — with $\Delta E^* \geq 3.3$ — on the color of resin composites tested.
(2) Admira and Durafill VS bleached with Whiteness HP containing 35% hydrogen peroxide yielded $\Delta E^* > 1$, a noticeable color change to the naked eye.

(3) Refractive indices of unbleached Admira and Durafill VS were found to be larger than that of Gradia Direct.
(4) Bleaching with carbamide peroxide gels increased the refractive index values of all the composites tested. However, the differing concentrations of these agents made no impact on the refractive index of Gradia Direct.
(5) Bleaching with 35% hydrogen peroxide had no effect on the refractive indices of Admira and Durafill VS, whereas it caused a considerable change to that of Gradia Direct.
(6) Color changes were found to be stronger in materials with larger refractive indices.

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