Effect of at-home bleaching with different thickeners and aging on physical properties of a nanocomposite

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ABSTRACT

Objective: To evaluate the influence of 16% carbamide peroxide (CP) containing different thickeners on the physical characteristics of a nanocomposite resin submitted or not to accelerated artificial aging (AAA). **Materials and Methods:** One hundred samples were randomly distributed into two groups ($n = 50$) according to AAA. Each group was divided into 5 subgroups ($n = 10$) depending on the bleaching/thickener treatment: CP + carbopol, CP + natrosol, carbopol, natrosol, and no treatment (control). The physical properties tested were color (ΔE), gloss (GU), mean roughness (Ra), and Knoop microhardness (KHN). The resin surface was performed with atomic force microscopy (AFM). **Statistical Analysis:** The color (variable ΔE) was assessed with two-way analysis of variance (ANOVA) and additionally with Tukey's and Dunnett's tests, the roughness values were submitted to Kruskal–Wallis, Dunn's, and Mann–Whitney's tests. Data on gloss and KHN were submitted to two-way ANOVA and Tukey's test ($\alpha = 0.05$). **Results:** Among the physical properties evaluated, CP + carbopol promoted a reduction in composite microhardness only, thus differing statistically from the controls. As for CP + natrosol, such a change was not observed. The aging process reduced all the physical properties, thus differing statistically from the nonaging group. CP + carbopol increased the roughness and decreased the gloss of aged resins, whereas natrosol reduced gloss only, which differed statistically from the controls. **Conclusions:** AFM showed evidence of the loss of organic matrix and exposure to load particles in the aged samples. Therefore, the replacement of carbopol with natrosol provided maintenance of the composite microhardness following bleaching. The aging process reduced the physical properties evaluated, and some changes were enhanced by the application of bleaching.

Key words: Accelerated aging, bleaching agents, color stability, composite resin, gloss, microhardness, surface roughness

INTRODUCTION

The technological development in the formulation of composite resins has provided better esthetic and mechanical results. With the use of nanotechnology, there has been a reduction in the size of load particles, which allows excellent polishing, greater resistance to wear, and improvement of optical characteristics.[1-3] This fact enables a more optimal esthetic treatment, with better mimetization between restoration and tooth. However, composite resins still have limitations, mainly regarding

the maintenance of physical and morphological properties over time.

With the esthetic valorization and the increasing search for dental bleaching, the possible alterations resulting from the action of bleaching agents on composite resins have been investigated. The increase in roughness, decrease in microhardness, reduction in adhesive interface strength, and changes in color and opacity are among the main alterations.[3-7] However, there is controversy in the literature regarding such alterations, and the results found tend to change depending on the composition of the composite resins, type of bleaching agent used, and concentration of peroxide, including frequency and length of application of these materials.[6,8-10]

In addition, the alterations resulting from the use of bleaching agents may not be related only to the application of peroxide but also to the presence of the thickening agent. The thickener is responsible for making the bleaching agent's liquid composition into gel, thus extending the release time of oxygen ions and keeping the product in close contact with dental surface.[11] Among the thickeners, carbopol is frequently used in the technique of at-home bleaching,[12] although this agent has been associated with alterations in the physical properties of composite resin such as reduction in microhardness.[13]

Natrosol is a thickener widely used in cosmetic and pharmaceutical industry as stabilizing and emulsifying agent as well, having broad pH stability and recommended for the use with acidic substances. In this way, its use has been proposed in the composition of whitening products. Therefore, in patients with direct esthetic restorations who are submitted to bleaching treatments, there is a direct contact between gel and restorative material. In this manner, studies that evaluate the action of bleaching gels on the composite resin are necessary as there is no consensus in the literature on the effect of these products on restorative materials including its action on aged resins within the oral cavity over time.[9]

In view of this, the aim of this study was to evaluate the influence of at-home bleaching containing different thickeners on the physical properties of a nanocomposite resin submitted or not to accelerated artificial aging (AAA). Two hypotheses null were tested in this study. (1) At-home bleaching would not affect the physical properties (e.g., gloss, color, roughness, and microhardness) of the restorative composite, regardless of the thickener used. (2) Aging of the material would not affect its properties following bleaching treatment.

MATERIALS AND METHODS

One hundred cylindrical samples containing nanocomposite resin (Filtek Z350 XT®, 3M/ESPE, Sumaré, SP, Brazil), measuring 7.0 mm in diameter and 2.0 mm in thickness, were prepared. The composite resin was inserted into the silicone matrix (Elite HD + normal setting-© Zhermack SpA-Badia Polesine [RO], Italy), which was previously made in one single increment using a metal spatula (Goldstein XTS flex, Hu-friedy, Chicago, USA). After insertion of the resin, the increment was covered with polyester strip and glass slide under a 500 g weight during 30 s. Samples were light-cured with a light emitting diode (LED) (Valo-Ultradent Products Inc., South Jordan, UT, USA) at irradiance 817 mW/cm² for 20 s.

Irradiance was previously calculated by measuring the power of light source (mW) with a powermeter (Ophir Laser Measurement, Jerusalem, Israel), whose result was then divided by the diameter of the LED light tip (cm²), which was measured with a digital caliper (Digital caliper, model CD-15C, Mitutoyo, Japan).

After preparing the samples, they were stored for 24 h at 37°C and 100% relative humidity. Next, the samples were submitted to the polishing process using a polishing machine (modelo APL-4; Arotec, Cotia, SP, Brazil). The top surface of each sample was polished for 1 min with #600, #1200, and #4000 grit silicon carbide sandpaper discs (CARBIMET Paper Discs; Buehler, IL, USA). Felt discs (TOP, RAM E SUPRA-Arotec, Cotia, SP, Brazil) in association with diamond pastes (3, ½, and ¼ µm) were used to finish the polishing process. An interval between each polishing using sandpaper and felt, the samples were cleaned for 5 min with deionized water in an ultrasonic bath (Ultra clear USC-1450A/Frequency 25 kHz, Unique, CE, Brazil) for removal of debris.

The samples were randomly distributed into two groups (*n* = 50) depending on the aging. Furthermore, each group was further divided into 5 subgroups (*n* = 10) according to the bleaching treatment and thickening agent [Table 1].

The AAA was performed in an EQ-UV natural (Equilam, Diadema, SP, Brazil) weathering device operating at controlled ultraviolet (UV) light radiation, which was

Table 1: Composition, manufacturer, lot number and pH value of the products used in the study

Materials	Composition	Manufacturer	Lot number	pH
Resin Filtek Supreme XT-shade A2E	Resin matrix: Bis-GMA, UDMA, TEGDMA and Bis-EMA Filler type: Nanoclusters (0.6 and 1.4 um), nanoparticle, zirconia, (5-20 nm) and silica (20 nm) Filler content (%): 78.5% (weight), 59.5% (volume)	3M/ESPE Sumaré, SP, Brazil	1333000736	-
Bleaching 16% carbamide peroxide + carbopol	Carbamide peroxide crystals 16%, deionized water QS, mint flavorant 1%, carbopol QSP 10 g	Drogal manipulation	660289B	Baseline: 6.52 After 4 h: 6.54
Bleaching 16% carbamide peroxide + natrosol	Carbamide peroxide crystals 16%, deionized water QS, mint flavorant 1%, natrosol QSP 10 g	Drogal manipulation	660289C	Baseline: 6.36 After 4 h: 6.54
Carbopol	Nostrabase® Gel anionic: Aqua, carbomero, disodium EDTA, phenoxyethanol and methylisothiazolinone, glycerin and polyacrylate glycerin, aminomethylpropanol	Drogal manipulation	660289A	Baseline: 6.36 After 4 h: 6.34
Natrosol	Nostrabase® Gel no ionic: Water, carbomero, disodium EDTA, phenoxyethanol and methylisothiazolinone, glycerin and polyacrylate glycerin, aminomethylpropanol	Drogal manipulation	6602289	Baseline: 5.85 After 4 h: 5.78

Bis-GMA: Bisphenol A diglycidyl methacrylate, UDMA: Urethane dimethacrylate, TEGDMA: Triethylene glycol dimethacrylate, Bis-EMA: Ethoxylated bisphenol A methacrylate, EDTA: Ethylenediaminetetraacetic acid

emitted from a xenon light source at 0.71 W/cm² and wavelength of 310 nm. The cycles consisted of 4 h exposure to UV-B light and 4-h condensation for a 300-h period at a constant temperature of 50°C.[14]

For application of different bleaching treatments and thickening agents, both aging and nonaging groups were subdivided into the following groups: 16% carbamide peroxide (CP) + carbopol, CP + natrosol, carbopol gel only, natrosol gel only, and nonbleaching treatment. The bleaching treatment was performed during 14 days. The bleaching was applied to the whole top surface of each sample. The samples were stored at temperature of 37°C ± 2°C for 4 h, thus simulating oral cavity. After each application, the samples were thoroughly washed under running water for 1 min for complete removal of gel from their surface, dried with absorbing paper, and then stored again at 37°C ± 2°C and 100% relative humidity until the next application. The samples receiving no treatment were also stored at temperature of 37°C ± 2°C and 100% relative throughout the experiment. The pH values of the bleaching gels were measured with a digital pH-meter for approximately 3 g of each gel [Table 1].

Color analysis
Color analysis was performed at the end of all treatments. The samples were placed on Teflon device (sample holder) inside a light cabin (GTI mini matcher MM1e; GTI Graphic Technology, Newburgh, NY, USA) to standardize the ambient light during the measurement process. The samples were submitted to color reading using a spectrophotometer (Konica Minolta CM-700d spectrophotometer Konica Minolta Investment, Shanghai, China) which was previously calibrated in accordance with to the manufacturer's instructions. The value of the without aging group

without bleaching was considered as a baseline for comparison with the other groups.

The values obtained were quantified using the Commission Internationale de L'E Clairage (CIE) lab system as three coordinates: L* (Luminosity, from 0 = black to 100 = white), a* (from axis - a = green to axis + a = red), and b* (from axis - b = blue to axis + b = yellow). These coordinates define the color of an object within a three-dimensional (3D) color space through the On-Color QC Lite software (Konica Minolta, Japan). Calculation of ΔE was obtained with the following formula: $\Delta E = ([L_1 - L_0]^2 + [a_1 - a_0]^2 + [b_1 - b_0]^2)^{1/2}$.

Gloss (GU)
For analysis of the gloss, a glossmeter (ZGM 1120 Glossmeter – Zehntner GmbH Testing Instruments, Switzerland) was used with light beam projecting on the sample's surface at a 60° angle (ISO-Standards, ISSO 2813), which allows the mean gloss to be evaluated. Four measurements were made, corresponding to each quadrant of the evaluated. The mean reading was recorded as a unit of gloss.

Roughness (Ra)
The surface roughness was evaluated using a rugosimeter (SV-3100S4 – Mitutoyo, Tokyo, Japan) and an atomic force microscope (Easy Scan 2, Nano surf, Boston, MA, USA). The rugosimeter was properly calibrated for reading in accordance with the ANSI requirements and equipped with a diamond tip (0.5 µm radius). The precision was of 0.01 µm, with cutoff value of 0.25 mm, reading length being 5 times the cut-off value (1.25 mm), and average speed of 0.1 mm/s. The samples were parallely placed on the surface of the equipment, marked with 3 equidistant points passing through the geometric center of the

sample to the border to guide the reading process. The readings were performed as follows: The first one at 180°, the second one at 135°, and the third one at 90°. The mean value of the three readings was considered as the final mean roughness value (Ra).

The atomic force microscope operated in the tapping mode, with constant variation between 31 and 71 N/m, wavelength of 225 µm, and resonance frequency of 160–210 kHz. 3D topographic and lock-in phase images (15 µm × 15 µm) were obtained using a profile meter mounted on the microscope. For quantitative analysis of the surface, the mean value of the three readings was considered as the final mean roughness value (Ra). For the qualitative analysis, all samples of each group were analyzed, and one topographic image and representatives lock-in phase images were randomly chosen for each treatment. The images were processed using the Gwyddion software (Gwyddion 2.29, GNU General Public License).

Knoop microhardness

For analysis of the Knoop microhardness (KHN), five indentations on the top surface of each sample were performed as follows: The first indentation was centrally made and the other four ones at a distance of 200 µm from the center. A KHN tester (HMV-2000, Shimadzu Corporation, Tokyo, Japan) with diamond indentator was used under a 50-g load for 15 s. The mean value of the five indentations was calculated as being the KHN value for each sample.

Statistical analysis

After exploratory and descriptive analysis using the SAS software (V. 9.2, 2010, SAS Institute Inc., Cary, NC, USA), the data were submitted to statistical tests. Data on gloss and microhardness were submitted to two-way analysis of variance and Tukey's test. Color was assessed through the variable ΔE on a factorial basis with additional treatment, whereas multiple comparisons were performed with Tukey's and Dunnett's tests. The data on surface roughness did not meet the assumptions for parametric analysis, and consequently, they were assessed using nonparametric Kruskal–Wallis's, Dunn's, and Mann–Whitney's tests. All the statistical tests were performed at the significant level of 5%.

RESULTS

Considering the values of microhardness listed in Table 2, it can be observed that statistically significant differences were found in aging groups compared with nonaging groups, with the latter having higher mean values ($\rho \leq 0.05$). No statistical differences were found between the different treatments in the aging group ($\rho \geq 0.05$). As for the nonaging groups, the treatment with carbopol had lower mean values of surface microhardness, statistically differing from the control group ($\rho \leq 0.05$) and natrosol and CP + natrosol groups ($\rho \leq 0.05$). However, the

Table 2: Mean values (standard deviation) of microhardness as a function of the treatment and aging process

Treatment	Aging process	
	Without	**With**
16% carbamide peroxide + carbopol	96.50 (6.17)[Abc]	58.83 (3.87)[Ba]
16% carbamide peroxide + natrosol	101.88 (4.50)[Aab]	57.15 (6.17)[Ba]
Carbopol	92.52 (5.70)[Ac]	56.07 (5.78)[Ba]
Natrosol	101.56 (4.68)[Aab]	58.33 (6.66)[Ba]
Without treatment	106.17 (4.43)[Aa]	62.41 (5.65)[Ba]

Mean values followed by different letters (uppercase letters in the lines and lowercase letters in the columns) indicate statistical differences ($\rho \leq 0.05$)

Table 3: Median values (minimum and maximum) of roughness as a function of the method, treatment, and aging process

Method	Treatment	Aging process	
		Without	**With**
Rugosimeter	16% carbamide peroxide + carbopol	0.184 (0.171; 0.199)*,[Bab]	1.232 (0.202; 1.749)*,[Aa]
	16% carbamide peroxide + natrosol	0.187 (0.172; 0.200)*,[Ba]	0.249 (0.206; 0.324)*,[Aab]
	Carbopol	0.178 (0.164; 0.198)*,[Bab]	0.220 (0.159; 0.297)*,[Ab]
	Natrosol	0.187 (0.175; 0.209)*,[Ba]	0.212 (0.160; 0.261)*,[Ab]
	Without treatment	0.170 (0.153; 0.183)*,[Bb]	0.216 (0.186; 0.284)*,[Ab]
AFM	16% carbamide peroxide + carbopol	0.010 (0.006; 0.013)[Ba]	0.284 (0.203; 0.335)[Aa]
	16% carbamide peroxide + natrosol	0.012 (0.008; 0.015)[Ba]	0.109 (0.076; 0.170)[Aab]
	Carbopol	0.018 (0.010; 0.056)[Ba]	0.074 (0.091; 0.053)[Ab]
	Natrosol	0.010 (0.003; 0.014)[Ba]	0.073 (0.057; 0.087)[Ab]
	Without treatment	0.011 (0.007; 0.013)[Ba]	0.095 (0.060; 0.193)[Ab]

Median values followed by different letters (uppercase letters in the lines and lowercase letters in the columns) indicate statistical differences ($\rho \leq 0.05$). *It differs from the AFM ($\rho \leq 0.05$). AFM: Atomic force microscopy

treatments with natrosol and CP + natrosol had values of microhardness similar to those of the control group, with no statistical difference ($\rho > 0.05$).

Table 3 shows the values of surface roughness (Ra) in μm obtained by the median (minimum and maximum) of different methods (i.e., rugosimeter and atomic force microscopy [AFM]) in function of treatments and aging. The roughness assessed using rugosimeter showed higher values, with statistically significant differences in the treatments and aging compared to analysis with AFM ($\rho \leq 0.05$).

Statistical differences in the aging groups and nonaging groups were found regarding surface roughness, regardless of the method of evaluation, with the former presenting higher mean values ($\rho \leq 0.05$). In the comparison between the treatments, the aging groups treated with CP + carbopol had higher roughness values compared to groups using carbopol, natrosol, and controls groups ($\rho \leq 0.05$). However, no statistical difference was found between CP + carbopol and CP + natrosol, which had an intermediate value ($\rho > 0.05$).

The nonaging groups, assessed with rugosimeter, showed that treatments with natrosol and CP + natrosol had higher roughness values compared to the control group ($\rho \leq 0.05$). The treatments with carbopol and CP + carbopol had intermediate values. On the other hand, AFM analysis showed no statistically significant difference ($\rho > 0.05$).

The results in Table 4 refer to the gloss on the surface. Lower mean values were found in all aging groups, statistically differing from the nonaging groups ($\rho \leq 0.05$). The comparison of different treatments between aging groups showed that CP + carbopol had lower surface gloss ($\rho \leq 0.05$). On the other hand, CP + natrosol had higher surface gloss compared to CP + carbopol but also had a lower gloss compared to groups treated with thickeners only (carbopol and natrosol) and controls. No significant differences were found between the latter groups ($\rho > 0.05$). Nonaging groups showed no statistical difference between them ($\rho > 0.05$).

The values listed in Table 5 refer to color change (ΔE). The highest mean values were found in all aging groups, statistically differing from the nonaging groups ($\rho \leq 0.05$). When the bleaching treatments were compared in the aging groups, a statistically significant difference ($\rho \leq 0.05$) was found as samples treated with CP had lower ΔE values compared to controls, regardless of the thickener. However, there

was no significant difference in the groups treated with thickeners only (i.e., carbopol and natrosol). In the nonaging groups, there was no statistically significant difference between them, although there was a difference compared to groups treated with thickeners only ($\rho \leq 0.05$).

3D images of the surface of the Filtek Z350 XT nanocomposite resin showed morphological alterations after 300 h of AAA [Figure 1], regardless of the treatment performed. This result was evidenced by the great difference measured between peak heights at the surface of these samples and regions with phase contrast in comparison to nonaging groups [Figure 2].

In the nonaging groups, small alterations in roughness were detected by AFM [Figure 2]. However, no difference was found in the phase images following bleaching treatment with thickeners [Figure 2a-d] compared to the control group [Figure 2e].

The aging group treated with CP + carbopol [Figure 1a] was found to have more alterations with more irregularities, which was demonstrated by the greater difference in the peak and valley heights on the surface of the samples. Furthermore, more regions with phase contrasts were observed due to color difference and phase image compared to other groups [Figure 1b-e].

**Table 4: Mean values (standard deviation) of gloss as a function of the treatment and aging process**

Treatment	Aging process	
	Without	With
16% carbamide peroxide + carbopol	87.68 (5.00)^{Aa}	3.70 (2.86)^{Bc}
16% carbamide peroxide + natrosol	89.94 (3.80)^{Aa}	21.76 (5.29)^{Bb}
Carbopol	89.90 (3.80)^{Aa}	39.30 (2.60)^{Ba}
Natrosol	89.90 (3.80)^{Aa}	39.43 (5.02)^{Ba}
Without treatment	89.96 (4.13)^{Aa}	35.39 (3.81)^{Ba}

Mean values followed by different letters (uppercase letters in the lines and lowercase letters in the columns) indicate statistical differences ($p \leq 0.05$)

Table 5: Mean values (standard deviation) of ΔE as a function of the treatment and aging process

Treatment	Aging process	
	Without	With
16% carbamide peroxide + carbopol	1.66 (0.48)^{Ba}	13.96 (1.29)*,^{Aa}
16% carbamide peroxide + natrosol	1.62 (0.53)^{Ba}	13.82 (0.54)*,^{Aa}
Carbopol	0.51 (0.29)^{Bc}	15.08 (0.78)^{Aa}
Natrosol	1.00 (0.27)^{Bb}	15.27 (1.04)^{Aa}
Without treatment	-	15.27 (0.65)

Mean values followed by different letters (uppercase letters in the lines and lowercase letters in the columns) indicate statistical differences ($p \leq 0.05$). *It differs from the without group with aging ($p \leq 0.05$)
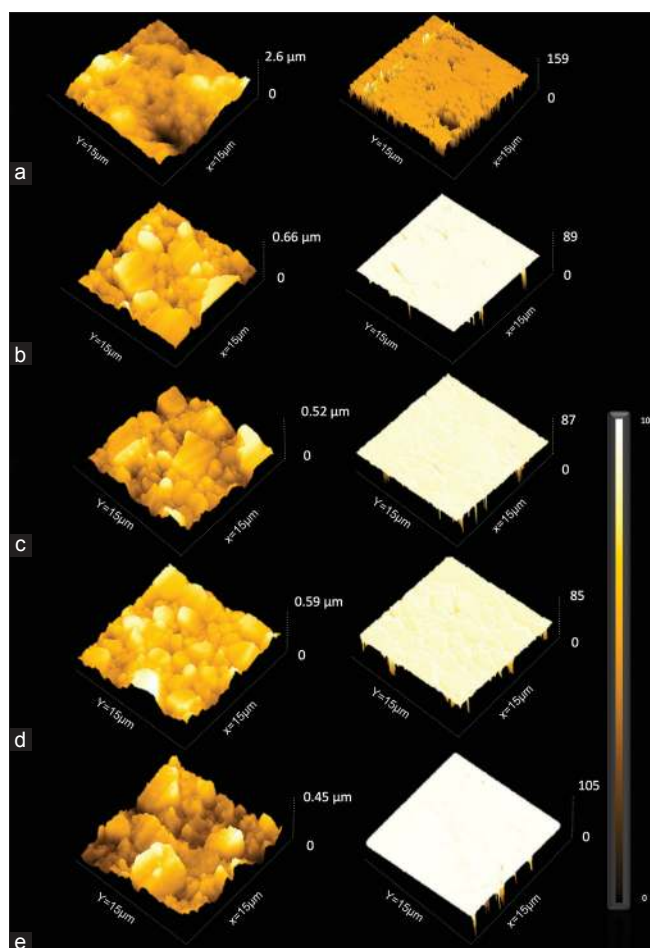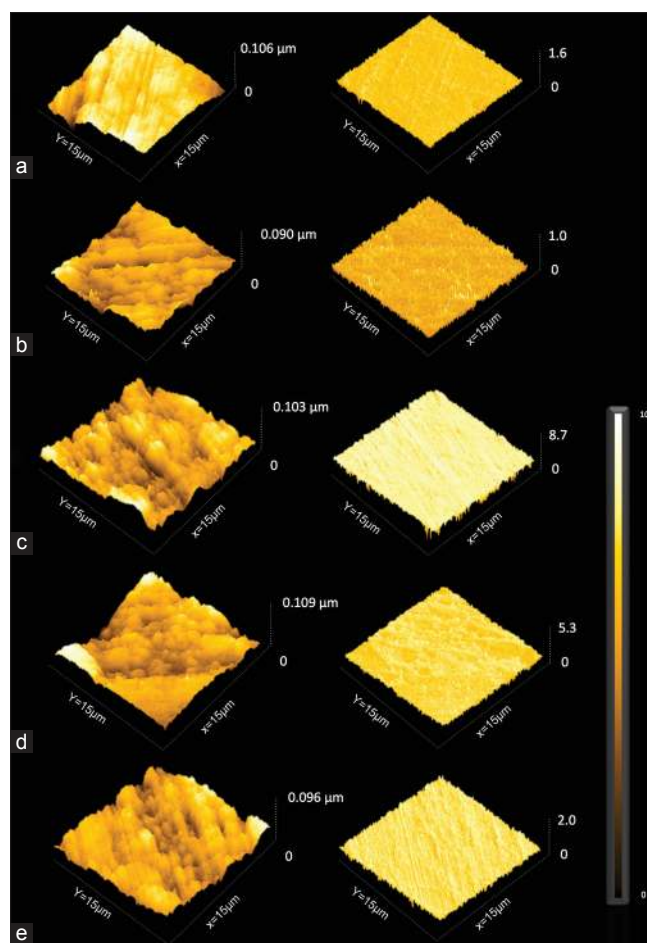
Figure 1: 3D topographic and lock-in phase images of composite resin surfaces without aging and the treatments produced by AFM: (a) 16% PC + carbopol (b) 16% PC + natrosol (c) carbopol, (d) natrosol, (e) without treatment – control (15 µm x 15 µm)

Figure 2: 3D topographic and lock-in phase images of composite resin surfaces with aging and the treatments produced by AFM: (a) 16% CP + carbopol, (b) 16% CP + natrosol, (c) carbopol, (d) natrosol, (e) without treatment – control (15 µm x 15 µm)

The assessment of aging groups treated with CP + natrosol [Figure 1b], and those treated with thickeners only [Figure 1c and d] showed similar result regarding the variations in the peak and valley heights as well as regions with phase contrast compared to aging groups without bleaching treatment [Figure 1e].

DISCUSSION

The null hypothesis tested in this study was partly accepted because the samples exposed to bleaching gel containing ionic thickener showed reduced micro-hardness values. In addition, the aging process did affect the properties evaluated, thus favoring the presence of more harmful effects on the resin composite following bleaching treatment.

The results showed that 16% CP + carbopol reduced the microhardness of the nanocomposite. This result is in accordance with Lima *et al.*,[13] who associated the presence of thickener (present in the CP-based

gels) with the decrease in the microhardness of resin-based materials, since the monomer bisphenol A-glycidyl methacrylate (Bis-GMA) is susceptible to solubility in the presence of carbopol. In this study, only application of carbopol to the surface of the composite resin was also capable of reducing the microhardness values compared to the control group.

Carbopol (carboxypolymethylene) is a synthetic hydrosoluble polymer used as gel-forming agent in aqueous systems to stabilize emulsions and to make solutions viscous.[12] The changes in the resin microhardness by carbopol have been attributed to its low pH[11] as this thickener is derived from a carboxylic acid, whose acidic pH can contribute to the composite degradation. Carbopol must be buffered to neutral pH to become inert before being inserted into the bleaching gel composition.[12] Therefore, the pH of the solutions was measured [Table 1], with carbopol being adequately neutralized and its acidic potential

disregarded in this study. Nevertheless, carbopol has high-ionic characteristics and can react with polymeric matrix components such as the monomers, particularly the Bis-GMA. According to Wu and Mckinney,[15] this monomer is highly susceptible to chemical softening because of the high levels of solubility, which can justify the result found.

Natrosol (hydroxyethylcellulose) is a cellulose-based polymer largely used in various materials such as latex emulsions, water-soluble resins, surfactants and detergents, anti-foaming agents, plastifying agents, and organic solvents as they have excellent compatibility with different types of composites. As a result, its use in bleaching was proposed because this polymer has nonionic characteristics and its use can be recommended in acidic substances as it has high pH stability (2.0–12.0). Thus, the results of this study demonstrated that natrosol used alone as well as in association with CP did not change the microhardness of the composite resin since no statistically differences were found compared to controls.

Microhardness was found to be decreased in all groups when dental composites were artificially aging. Artificial aging was used to allow material degradation to be analyzed in a short time, that is, corresponding to months or years within the oral cavity. The aging effect is observed through the action of both UV radiation and water on the polymer plastification. According to Ferracane,[16] plastification is the result of the presence of water inside the matrix or at the matrix/load particle interface, causing relaxation or softening of the bonds, which reduces the microhardness of the composite resin. However, no statistical differences were found between the different bleaching treatments and controls regarding the microhardness of the composite after artificial aging. Thus, it was found that application of bleaching gels was not able to enhance the decrease of microhardness caused by artificial aging.

With regard to the surface roughness, it was possible to observe statistically significant differences between the different methods used, since higher roughness values were found in the analysis using rugosimeter compared to that using AFM.

Roughness readings are strongly influenced by the radius and precision of the tip onto the surface and hardness of the material.[17] The greater the tip radius, the lower the detection of the mean surface roughness value obtained, and the higher the roughness value

expected.[18] The rugosimeter has a tip of 0.5 μm radius, whereas AFM has a tip of approximately 10 nm (0.01 μm). This explains why AFM can achieve a more precise determination by detecting smaller surface irregularities in the different groups, allowing better estimation of the mean surface roughness (Ra) at a nanometric scale.

With regard to the reading length, the scanning provided by the rugosimeter occurs linearly, that is, along one axis only, and in this study, the reading length was of 1.25 mm. On the other hand, the AFM scanning occurs along two axes (X and Y) and consequently provides a better image for visualization of the topography of the sample. In this study, a total of 256 scans of 15 μm per image were performed, which corresponds to 3.84 mm of scanned area. Therefore, the set of measurements were greater in the AFM, which decreases the statistical errors.

Although statistical differences have been found in the nonaging groups using rugosimeter, statistical differences were also found in the nonaging groups as the treatments with CP + natrosol and natrosol only showed higher mean values compared to controls, but with no statistical differences compared to treatments with CP + carbopol and carbopol only. In the AFM, no statistical differences were found. However, despite the differences found in the groups, the roughness values were lower than 0.2 μm [Table 3 and Figure 2], which characterizes a low-roughness surface. In addition, this value is considered the threshold for bacterial adhesion.[19]

This change in roughness by the treatment with bleaching gel + natrosol did not affect the surface gloss of the composite resin, a result also observed in all other treatments without aged resin. This may be attributed to the homogeneity between matrix and load particle at the surface of the nanocomposite. This resin has an inorganic portion consisting of weakly bonded aggregates of silicone nanoparticles (SIO_2) and zirconium-silica (SIO_2/ZrO), thus forming agglomerates or nanoclusters. This fact allows a greater amount of load particles to be inserted, which are then distributed throughout the whole matrix. This, in turn, decreases the formation of areas made up of organic matrix only, making the resin more unstable to chemical agents.[20] Therefore, composites with uniform surface in relation to the quantity of matrix and charges can suffer minor changes resulting from the action of bleaching agents. In addition, the formation of clusters allows them to be eroded and

not necessarily removed during the polishing process, which enables excellent surface finishing[21] and gloss.

Groups submitted to AAA had higher roughness values in both methods, as well as lower gloss values. This happened because the aging process using light and condensation has possibly degraded the organic matrix of the resin, resulting in leaching of inorganic components [Figure 2], which may have contributed to an increase in the porosity.[22] Therefore, the surface gloss is directly influenced by the roughness. Studies show that the light beam inciding on a smooth surface is directly reflected at a defined angle, whereas on a rough surface the light beam is reflected at several angles, that is, on a diffuse basis.[23,24] Therefore, part of the light inciding on the rough surface is dissipated, resulting in a lower gloss value.

When different bleaching treatments were evaluated in the aging groups, the use of CP + carbopol had higher roughness values and lower gloss values compared to control group. Rattacaso *et al.*[22] demonstrated that changes in the resin's surface resulting from bleaching agents occur due to the action of free radicals, high oxidative capacity, and the presence of water. The latter is the by-product from the dissociation of hydrogen peroxide, which can accelerate hydrophilic degradation of the resin and disorganize the matrix, thus increasing roughness and altering the surface gloss. On the other hand, the group treated with CP + natrosol had lower gloss values, with statistically significant difference compared with control group and groups with thickeners (carbopol and natrosol). However, when compared to the group treated with CP + carbopol, higher gloss values were found. This result suggests that the use of CP + natrosol is more likely to be effective in the maintenance of the surface gloss.

Application of only thickeners affected neither gloss nor roughness of the aged samples. Statistically significant differences were not found in these groups in relation to controls. This fact leads us to understand that thickeners alone cannot change significantly the surface of the composite, as to change the brightness and the roughness. However, the synergetic action of both thickeners and free radicals released by peroxide decomposition can enhance the organic degradation of the polymeric matrix and consequently impair the surface gloss, particularly in association with ionic thickener.

The color of the resin was assessed according to the CIE system (L*a*b*), which quantifies the general color variation (ΔE). According to Janda *et al.*,[25] when ΔE =0–2, the color change is clinically imperceptible; ΔE = 2–3, color change is little perceptible; ΔE > 3–8, the color change is moderately perceptible; and ΔE >8, the color change is intensively perceptible. The results of this study show that variation in color was very small and clinically imperceptible in the nonaging group, regardless of the treatment used (ΔE < 2). Therefore, different bleaching treatments were not able to alter the color of the aged samples.

Groups submitted to AAA showed significant changes in color, regardless of the treatment. Variation in color was found to be intensively perceptible (ΔE = 13), which occurred due to physical-chemical reactions unleashed by UV light radiation.[26] This may be attributed to several factors such as the presence of residual camphorquinone,[27] a yellow-colored co-initiator degrading over time and which promotes changes in the color of the composite,[28] even when used in small amounts from 0.03% to 0.1%; oxidation of tertiary amines (co-initiators), which form by-products derived from light activation (these activated molecules can react with oxygen, aromatic groups, or small organic molecules incorporated during manipulation of the material, resulting in the formation of a system called chromosphere, which increases the absorption of visible light and yellows the material under influence of light and heat.[29,30] All these conditions were present in the AAA process used in this study. Furthermore, the darkening of the composite resin following AAA may still be attributed to the hydrophilic characteristics of the monomers present in the resin. There is a difference in hydrophilicity between the matrix monomers, with the degree of difference being presented in the following order: TEGDMA > Bis-GMA > Bis-EMA > UDMA > HMDMA.[31] Among these, Bis-GMA and triethylene glycol dimethacrylate (TEGDMA) have water absorption rates of 3–6% and 0–1%, respectively. Thus, it was expected that there was a considerable sorption of water by the resin in this study. In addition to Bis-EMA and urethane dimethacrylate, resin matrix is predominantly composed of monomers that are more susceptible to hydrolysis, i.e., 10–15% of Bis-GMA and 10–15% of TEGDMA,[32] with water absorption rates of 3–6% and 0–1%, respectively.[7] In fact, the presence of water leads to changes in the color of the resin, a consequence of the alteration in the light refraction index.[33]

When aging groups were treated with CP, regardless of the thickener, lower values of ΔE were observed, thus

demonstrating that surface degradation promoted a subtle change in the color of the composite. Therefore, we understand that the replacement of the thickening agent did not interfere with the color in these groups. In general, when exposed to bleaching treatments, the color change mechanism in the composite resin includes oxidation of surface pigments, oxidation of amines (which are responsible for color stability over time), or breakdown of the resin matrix (through leaching of monomers).[7,34] These factors seem to explain this slight variation in color reported in this study. Dental composite can absorb water and chemical products through both polymeric matrix and matrix-charge interface, resulting in the softening of the material. This can favor the leaching of components in its structure, which enhances its degradation[3,8,35,36] and makes the color of the composite lighter. In addition, studies have reported that changes in temperature and humidity can promote greater degradation in composites aged under various physical-chemical conditions (e.g., visible light and UV irradiation), which favors deeper penetration of the bleaching agent through microfractures in the restorations.[8,35] Therefore, a greater loss of organic and inorganic material from the surface may have resulted in color change, making the samples lighter in these groups.

The samples were qualitatively analyzed for morphological changes in their surfaces using AFM. This methodology allows the materials to be structurally characterized through visualization of high-resolution 3D topographic and lock-in phase images.[2]

For the nonaged samples, regardless of the bleaching treatment, the AFM cantilever sensor showed small alterations in roughness, although no significant irregularity and no difference were found in the phase images following bleaching treatment with thickeners [Figure 2a-e]. A low-roughness surface was observed in this study, which was similar to that in all groups, even after bleaching treatments [Figure 2a-e]. This result allows us to state that bleaching treatments had minimal effects on the samples.

The aging groups showed higher roughness [Figure 1a-e]. The variation demonstrated in the roughness tests, and 3D topographic images revealed a surface roughness of 0.2 μm, even areas above 1 μm following AAA. Bollen *et al.*[37] reported that values above 0.2 μm contribute to plaque accumulation, which in turn increases the risk of caries lesion and periodontal diseases. Therefore, from the clinical view, aged composites can compromise the material's longevity and the patient's oral health.

However, the aging group treated with CP + carbopol [Figure 1a] showed higher roughness values and phase-contrast regions. This demonstrates that this group was found to have a more pronounced loss of resin matrix and exposure to load particles in comparison to other groups, whose roughness were lower and few phase-contrast regions [Figure 1b-e].

Based on the results of this study, one can find that aged composite resin has produced relevant changes in the physical properties evaluated. Furthermore, some effects were enhanced after application of bleaching agents, thus compromising esthetic aspects regarding these materials. As for without aging composites, changes were found to be minimal and dependent on the type of bleaching agent, which might have suggested a judicious selection of the bleaching product, since the microhardness values were reduced in some compositions.

CONCLUSION

Changes in the physical properties of the nanocomposite by whitening agents vary depending on the thickener used. The replacement of carbopol with natrosol has provided maintenance of the microhardness of the composite following whitening, whereas the aging process reduced all the physical properties evaluated, and some changes were enhanced by the application of bleaching.

Conflicts of interest
The authors of this manuscript certify that they have no proprietary, financial, or other personal interest of any nature or kind in any product, service, and/or company that is presented in this article.

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