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Degradation of optical and surface properties of resin-based composites with distinct nanoparticle sizes but equivalent surface area

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ABSTRACT

Objective: To determine the optical and surface properties of model resin-based composites made with distinct nanoparticle sizes but equalized surface area, among them, before and after ageing.
Methods: Model resin-based composites based on BisGMA/TEGDMA (50:50 mol%) were loaded with three different fumed silica filler content (7 nm/examethyldisilazane, 12 nm/octylsilane, and 16 nm/dimethylchlorosilane), but with equivalent surface area (BET method). The optical and surface properties of the disk-shaped specimens were measured in 24 h after photoactivation (baseline) and repeated after water storage (90 days at 37 °C), and after abrasion (20,000 cycles of brushing). CIELAB individual parameters, color difference (ΔE^*_{ab}), translucency parameter (TP), gloss (G.U.) and roughness (*Ra* parameter) were measured. Data were statistically analyzed at α=0.05 significance level.
Results: CIE L^* and TP were not affected by ageing in any group. CIE a^* was increased and CIE b^* decreased for the 12 nm and 16 nm groups and did not show any difference for the 7 nm group. After ageing, the lowest ΔE^*_{ab} was observed for the 7 nm group. Gloss and roughness were statistically equivalent for all groups, before and after ageing. The water storage didn't show any significant difference while the abrasion decreased gloss and increased the roughness.
Conclusion: The optical properties of the tested materials were not dependent of the fillers' surface area, while the surface properties were.
Clinical significance: Several factors influence the ageing resistance of the resin-based composites, including the surface area of the fillers and the amount and coupling treatment of them. The improvement of the material's physical stability could avoid the premature replacement of dental restorations.

1. Introduction

Dental resin-based composites are constituted by organic and inorganic components. The organic phase comprises different molecular weight monomers that polymerize to produce a polymer matrix. The inorganic content is generally composed of ceramic oxides and/or glass fillers [1] and their morphology is directly associated with the material's physical properties as well as handling properties [2]. A coupling agent (usually an organo-silane) binds the polymeric matrix with the inorganic components.

The inorganic content has been purposely reduced in size to facilitate surface polishing and reduce wear damage [1,3]. It has been suggested that the dispersion of nanofillers into the polymeric matrix improves the material's physical properties after photo-activation [3–5]. However, nano-structured resin-based composites are very difficult to process with conventional techniques. There is a strong tendency for filler agglomeration due to stronger hydrogen bonding by hydroxyl groups and high surface free energy. The smaller the filler, the more difficult it becomes to break down these agglomerates to yield a homogeneous

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distribution within the polymeric matrix [6]. The particle agglomeration might also be influenced by the coupling agent type and fraction [7].

From a clinical perspective, a highly stable appearance can increase the longevity of restorations. The optical and the surface properties of resin-based composites can be modified by several factors such as wear, degradation of the polymeric matrix or filler components, and weakening of matrix-filler bonding. Several studies have focused on the effect of filler type, shape, and size on the resin-based composites' overall appearance as well as their ageing resistance [8–10]. In a previous study [9], nano-structured resin-based composites were made with three different silanized fumed silica fillers (7 nm, 12 nm, and 16 nm average sizes) dispersed into a monomeric matrix with the same mass content. The filler size had a significant influence on the optical and surface properties of the composites. The smallest filler size material showed improved color stability and gloss retention. However, this resulted in different handling characteristics among the groups due to the surface energy of the different fillers.

Though the size of fillers in dental resin-based composites has been the subject of many articles, the surface area of the fillers has not been accounted for, with respect to the overall appearance. Therefore additional studies are required to analyze the optical and surface properties of resin-based composites when the filler surface area is kept constant. The objective of this study was to evaluate the optical properties, by the CIELAB individual parameters, the CIELAB color difference, and the translucency parameter, as well as surface properties, by the gloss and the roughness, of model resin-based composites formulated with different filler size but having equivalent surface area, before and after ageing procedures. The hypotheses were that the model resin-based composites with different filler sizes but equivalent surface area would show (i) similar effects on optical properties after ageing, and (ii) similar effects on surface properties after ageing.

2. Materials and methods

2.1. Experimental design

This *in vitro* 3 × 3 factorial-designed study (n = 6) evaluated two factors: filler content (7 nm, 12 nm, and 16 nm) and ageing conditions (baseline, water storage and surface abrasion). The optical and surface property measurements were performed at the three ageing conditions: a) 24 h after a curing period in dry and dark storage (baseline); b) after the immersion of all specimens in distilled water at 37 °C for 90 days, and c) after toothbrush abrasion of the top surface of the specimens. The sample size was based on previous study [9]. The collected response variables were CIELAB individual parameters (CIE L^*, CIE a^*, and CIE b^*), translucency parameter, CIELAB color difference (ΔE^*_{ab}), gloss, and roughness.

2.2. Surface area measurements and composite formulation

Three different silanized hydrophobic fumed silica fillers with average filler diameter of 7 nm (hexamethyldisilazane; Aerosil® R 812, Evonik Industries, Germany), 12 nm (octylsilane; Aerosil® R 805, Evonik), and 16 nm (dimethylchlorosilane; Aerosil® R 972, Evonik) were selected for this study (Table 1). The surface area of each filler type was determined by the BET method [11], with the use of a surface area analyzer (Quantasorb QS-9, Quantachrome Instruments FL, USA). The obtained BET surface area values for each filler particle, presented in Table 1, were in accordance to those reported by the manufacturer.

The model composites were prepared with a polymeric matrix composed of 2,2 bis[4-2(2-hydroxy-3-methacroyloxypropoxy) phenyl] propane (BisGMA, Esstech Inc., Essington, PA, USA) and triethyleneglycol dimethacrylate (TEGDMA, Esstech Inc.) in a 50:50 weight ratio. Camphorquinone at 0.5 mol% (Esstech Inc.) associated with ethyl 4-dimethylaminobenzoate at 0.9 mol% (Sigma-Aldrich, Chemie, Steinheim, Germany) were added as the photo-initiator:co-initiator system, based on a previous study [12].

In order to equalize the total surface area among each of the different filler particles, the model resin-based composites were formulated with different weights of filler, as shown in Table 1. Filler loading for the higher average particle size (16 nm) was set at 45.5 wt% based on a previous study [9] where the same fillers were tested. Then the other filler fractions (7 nm and 12 nm) were proportionally reduced. All components were weighed with 0.0001 g accuracy using an analytical balance (AX 200, Shimadzu Corporation, Tokyo, Japan), and were mechanically mixed (DAC 150 Speed Mixer, Flacktek, SC, USA) for 1 min to produce a homogeneous paste.

Six disc-shaped specimens were made for each group in a cylindrical metal mold of 8-mm inner diameter and 2-mm thickness. After the composite insertion, the top surface was covered with a Mylar strip and made flat by pressing down with a glass slab. The specimens were light cured from the top surface for 40 s using a LED curing unit (Radii CAL, SDI, USA) operated in standard mode with irradiance of 1000 mW/cm^2, as measured with a hand-held radiometer (LED radiometer, Demetron, Kerr, WI, USA). Then, all specimens were mechanically polished on both surfaces with the use of a grinding/polishing machine (MetaServ 250, Buehler, IL, USA) with 2000 and 4000-grit SiC paper under continuous water cooling.

A toothbrush simulating machine (MEV2, Odeme, SP, Brazil) was used to abrade the specimens' top surface [9]. Soft toothbrushes (Colgate Professional Extra Clean, Colgate-Palmolive Company, SP, Brazil) were fixed in a toothbrush holder so that all the bristles were in contact with the specimen. The machine was adjusted to apply 2.5 N of vertical load on the specimens during horizontal movements of the toothbrush throughout the test. A popular dentifrice (Colgate Total 12 Clean Mint, Colgate-Palmolive Company) was used to form the slurry (2:1, water: toothpaste) according to ISO/TS 1469-1. Each "station" of the machine was filled with 5 ml of slurry. All specimens were brushed with 20,000 cycles, which corresponds to approximately 2 years of toothbrushing [13]. The toothbrushes and the slurry were replaced for each specimen every 2500 cycles. After the abrasion, the specimens were removed from the machine, rinsed with tap water, cleaned in an ultrasonic bath with distilled water for 5 min, and gently air dried.

Table 1
Characteristics of the filler particles and formulation of the dental composites tested.

Average filler size	Filler coupling agent	Surface area (BET method)	Filler fraction (wt%)	Polymeric matrix fraction (wt%)	Polymeric matrix formulation
7 nm	hexamethyldisilazane	246 m^2/g	15.5	84.5	BisGMA/TEGDMA (50:50 mol%),
12 nm	octylsilane	178 m^2/g	32.0	68.0	camphorquinone (0.5 mol%),
16 nm	dimethyldichlorosilane	135 m^2/g	45.5	54.5	ethyl 4-dimethylaminobenzoate (0.9 mol%)

All fillers were from Evonik, Germany. BisGMA, TEGDMA, and CQ were from Esstech Inc., USA. EDMAB was from Sigma-Aldrich, Germany.

2.3. SEM analyses

Three specimens of each group were carbon-coated prior to scanning electron microscopy (SEM) analysis at 10,000× magnification (JSM-6610, JEOL Ltd., Tokyo, Japan). Images were recorded prior to and after ageing (after water storage and surface abrasion).

2.4. Optical properties measurements

Color was measured according to the CIELAB individual parameters in the SCI mode [14], over a zero calibrating box (CIE L^* = 0.0, CIE a^* = 0.0, and CIE b^* = 0.0), a white background (CIE L^* = 93.2, CIE a^* = −0.3, and CIE b^* = 1.6) and a black background (CIE L^* = 0.5, CIE a^* = 0.7, and CIE b^* = −0.6) using a spectrophotometer with illuminating/measuring geometry d/8° (CM-2600d, Konica Minolta, Japan). The measuring aperture was 6 mm in diameter. Illuminating and viewing configurations complied with CIE 10° observer geometry and D65 illuminant. An average of three readings in the center of the top surface for each specimen was calculated. The CIE L^*, CIE a^*, and CIE b^* values were automatically calculated by the software. The CIE L^* axis is the lightness, where 100 is white and 0 is black. The axes CIE a^* and CIE b^* are respectively the red-green and yellow-blue chromaticity coordinates.

The translucency parameter (TP) was calculated by the formula [15]:

$$TP = [(L^*_w - L^*_b)^2 + (a^*_w - a^*_b)^2 + (b^*_w - b^*_b)^2]^{1/2}$$

where the subscript "w" refers to the CIELAB values for each specimen over the white background and the subscript "b" refers to the CIELAB values for same specimen over the black background. The CIELAB color difference (ΔE^*_{ab}) was calculated using the CIELAB values over the white background by the formula [16]:

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

where ΔL^*, Δa^* and Δb^* are the mathematical differences between CIE L^*, CIE a^* and CIE b^* of the different measurement periods (water storage and surface abrasion) with the baseline (24 h after curing).

2.5. Surface property measurements

The gloss measurement was performed with a glossmeter (ZGM 1110, Zehntner, Switzerland) which was calibrated against a black glass standard provided by the manufacturer. Measurements were performed at 60° light incidence and reflection angles relative to the vertical axis [17]. The average of four readings performed on the center of the top surface for each specimen was calculated. The measuring window was 4.7 mm × 2 mm.

The roughness measurement was performed with a surface profiler (SJ-201, Mitutoyo, Japan). The diamond stylus was traversed at a constant speed of 1 mm/s across the surface with a force of 6 mN. The cut-off length was 0.25 mm and the measuring length was 2 mm. The average of six line scans performed per top surface of each specimen was calculated, three in the horizontal and three in the perpendicular direction. The amplitude parameter R_a, which relates the arithmetic mean between the peaks and valleys of the surface, was used.

2.6. Statistical analyses

Statistical analyses were conducted using SigmaPlot® 13.0 software (Systat Software, San Jose, CA, USA). Data for the CIELAB individual parameters, TP, gloss, and roughness were analyzed by two-way repeated measures analysis of variance (one factor repetition), considering filler content and ageing condition as factors. Data for ΔE^*_{ab} was analyzed by two-way analysis of variance, considering filler content and ageing condition as factors. The gloss and roughness data were heteroscedastic and thus were transformed to ranks prior to statistical analysis. All pairwise multiple comparisons procedures were performed using the Student-Newman-Keuls' method (α = 0.05).

3. Results

The CIE L^*, CIE a^*, CIE b^*, and the TP values for each ageing condition are presented in Table 2. For CIE L^*, the factor filler size was statistically significant ($p < 0.001$) while the ageing condition was not ($p = 0.092$), nor was the interaction between factors ($p = 0.067$). The 7 nm group showed the highest values ($p < 0.001$), representing the highest luminosity, followed by the 12 nm group and then the 16 nm group ($p < 0.001$) in all ageing conditions.

For CIE a*, filler size, ageing condition, and their interaction were statistically significant ($p < 0.001$). At the baseline, the 7 nm group showed higher values than the 12 nm group ($p = 0.004$) which showed higher values than the 16 nm group ($p < 0.001$). At both other ageing conditions, the 12 nm group showed the highest values ($p = 0.002$), and there were no differences between the 7 nm and 16 nm groups ($p = 0.360$). The water storage significantly increased the values for the 12 nm and 16 nm groups ($p < 0.001$), representing a redness effect, but had no difference for the 7 nm group ($p = 0.361$). The surface abrasion caused no significant difference in any groups ($p = 0.287$).

For CIE b*, filler size and ageing condition as well their interaction were also statistically significant ($p < 0.001$). In all ageing conditions the 7 nm group showed the highest values ($p < 0.001$), followed by the 12 nm group, and the 16 nm group the lowest ($p < 0.001$). The water storage decreased the values for the 12 nm ($p = 0.003$) and 16 nm group ($p < 0.001$), representing a blueness effect, and had no difference for the 7 nm group ($p = 0.192$). The surface abrasion caused no significant difference in any group ($p = 0.344$).

For TP, filler size ($p < 0.001$) and ageing condition ($p < 0.001$) as well their interaction ($p = 0.010$) were also statistically significant. In all ageing conditions the 7 nm group showed the highest values ($p < 0.001$), followed by the 12 nm group, and the 16 nm group the lowest ($p < 0.001$). The water storage did not influence any group ($p = 0.188$), nor did the surface abrasion ($p = 0.170$).

Table 2
Results of the optical properties measurements (n = 6). Values are means ± standard deviations. Over white background CIELAB individual parameters and translucency parameter (TP) values at the three ageing conditions: baseline (24 h after curing), water storage (after 90 days of distilled water storage at 37 °C), and surface abrasion (after 20,000 cycles of brushing).

	Group	Baseline	Water storage	Water storage + surface abrasion
CIE L^*	7 nm	76.8 ± 0.7 ^{Aa}	77.0 ± 1.0 ^{Aa}	76.0 ± 1.3 ^{Aa}
	12 nm	72.7 ± 0.9 ^{Ab}	73.5 ± 1.1 ^{Ab}	73.3 ± 0.8 ^{Ab}
	16 nm	71.7 ± 0.3 ^{Ac}	71.8 ± 0.3 ^{Ac}	71.6 ± 0.5 ^{Ac}
CIE a^*	7 nm	2.5 ± 0.1 ^{Aa}	2.4 ± 0.1 ^{Ab}	2.4 ± 0.1 ^{Ab}
	12 nm	2.1 ± 0.3 ^{Bb}	2.78 ± 0.2 ^{Aa}	2.7 ± 0.2 ^{Aa}
	16 nm	1.2 ± 0.3 ^{Bc}	2.4 ± 0.3 ^{Ab}	2.3 ± 0.2 ^{Ab}
CIE b^*	7 nm	12.7 ± 0.6 ^{Aa}	13.2 ± 0.8 ^{Aa}	13.0 ± 0.9 ^{Aa}
	12 nm	11.4 ± 1.0 ^{Ab}	10.5 ± 0.7 ^{Bb}	10.4 ± 0.8 ^{Bb}
	16 nm	4.5 ± 0.4 ^{Ac}	1.3 ± 0.4 ^{Bc}	1.0 ± 0.5 ^{Bc}
TP	7 nm	38.7 ± 1.1 ^{Aa}	39.5 ± 1.4 ^{Aa}	38.9 ± 1.7 ^{Aa}
	12 nm	32.5 ± 1.6 ^{Ab}	34.3 ± 1.6 ^{Ab}	35.0 ± 1.7 ^{Ab}
	16 nm	24.7 ± 0.8 ^{Ac}	25.1 ± 0.5 ^{Ac}	25.2 ± 1.1 ^{Ac}

In each row, distinct capital letters indicate significant difference among the ageing condition while distinct lowercase letters in each column, indicate significant difference among filler size groups (α = 0.05).

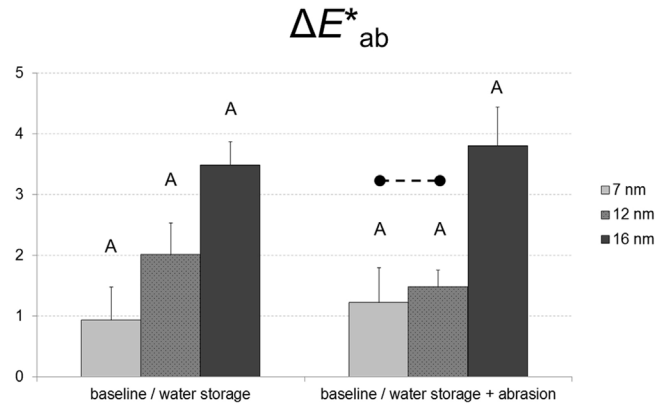

Fig. 1. Results of ΔE^*_{ab} (n = 6). Bars are mean + standard deviations. Similar letters indicate no statistical difference for each group in both periods. Statistically similar groups are indicated by connected dots above bars.

The ΔE^*_{ab} values are shown in Fig. 1. The filler size factor was statistically significant ($p < 0.001$) while the ageing condition ($p = 0.796$) and the interaction between the factors were not. After water storage, the 16 nm group showed the highest value ($p < 0.001$), followed by the 12 nm group ($p = 0.002$), and then by the 7 nm group ($p < 0.001$). After the surface abrasion, the 16 nm group also showed the highest value ($p < 0.001$), followed by the two other groups that were statistically equivalent ($p = 0.244$).

The surface property measurements are shown in Table 3. The gloss and roughness values are shown for each ageing condition. For the gloss, the factor filler size wasn't statistically significant ($p = 0.659$) while the ageing condition factor was ($p < 0.001$). The interaction between factors wasn't significant ($p = 0.088$). There were no observed differences among the groups in any ageing condition ($p = 0.136$). The water storage had no difference in any group, but the surface abrasion decreased the values for all groups ($p < 0.001$).

Regarding the roughness, the filler size factor wasn't statistically significant ($p = 0.080$) while the ageing condition ($p < 0.001$) and the interaction between factors ($p = 0.048$) were. There were no observed differences among the groups in any ageing condition ($p = 0.331$). The water storage had no difference in any group, but the surface abrasion decreased the values for all groups ($p < 0.001$).

The SEM images (Fig. 2) of all groups at baseline and after ageing, show the filler agglomeration and the filler-matrix morphology of each experimental composite. Different filler clusters were observed for each average filler size. Although this distinction is more evident for the 7 nm group, all clusters were homogeneously distributed. The cluster sizes ranged up to 487 nm for the 7 nm group, 958 nm for the 12 nm group, and 1545 nm for the 16 nm group. After ageing, different surface patterns were observed. The decrease of clusters was more evident in the 12 nm group.

4. Discussion

Ageing of resin-based composites takes place due to several factors. In the currently study three different filler types, with distinct average size and silane treatment, were added into the polymeric matrix at different masses in order to equalize the overall surface area of the fillers. It was expected that ageing would have similar effects on optical properties. However this was not observed and, consequently, the first research hypothesis was rejected.

The measurement of color of a resin-based composite can be objectively achieved by the CIELAB individual parameters. For the CIE L^* parameter, the 7 nm group was higher than the 12 nm group, which in turn was higher than the 16 nm group. This can be attributed to the translucency of each resin-based composite material. Considering that the color measurements were made over a white background, the higher the material's translucency, the higher the CIE L^*. It was also observed that the CIE L^* was not influenced by ageing. Regarding The CIE a^* and b^* parameters, the 7 nm group also showed higher values than the 12 nm group, which in turn showed higher values than the 16 nm group. This may be related to the different inorganic fractions of each group. The water storage increased the CIE a^*, redness, and decreased the CIE b^*, blueness, for the 12 nm and 16 nm groups, but no significant changes were observed for the 7 nm group. The redness and the blueness effects due to water storage were also reported in other studies [9,18,19]. These changes could be related to a number of factors, including the water uptake by the filler-matrix interface [20], the oxidation products forming from the amine co-initiator [12], the colored peroxide products formed by oxidation reactions of unreacted C=C double bonds [21], the degradation of the silane coupling agent and reinforcing filler [7,22], the leaching of unreacted monomers caused by hydrolysis [9,12,23], and the photoinitiator components that were not consumed during light exposure [19].

As reported by Kalachandra [24], water penetrates within the polymer chains and is accommodated in the interface between the inorganic filler and the organic matrix. The water uptake depends on the filler type, coupling agent type and differences in filler-matrix bond strengths. It decreases when there is most effective coupling between filler and matrix. This was also verified by Kalachandra and Wilson [20], who observed lower diffusion coefficient ratios in unfilled compared to filled resin-based composites. In the present study, the group with highest inorganic content ratio by weight (16 nm) presented the higher color difference while that with the lowest (7 nm) showed the highest color stability. Although the water uptake rate wasn't determined in the current research, the enhanced color change for the composite with the highest filler content in this study is not consistent with the results of Kalachandra and Wilson [20], who showed that the composites which absorbed the most water, and consequently presented the greatest decline in elastic modulus,

Table 3
Results of the surface properties measurements (n = 6). Values are means ± standard deviations. Gloss and roughness values at the three ageing conditions: baseline (24 h after curing), water storage (after 90 days of distilled water storage at 37 °C), and surface abrasion (after 20,000 cycles of brushing).

	Group	Baseline	Water storage	Water storage + surface abrasion
Gloss	7 nm	84.6 ± 6.0^{Aa}	$87,5 \pm 5.74^{Aa}$	72.3 ± 5.5^{Ba}
	12 nm	88.8 ± 4.6^{Aa}	89.2 ± 1.87^{Aa}	61.3 ± 5.0^{Ba}
	16 nm	89.2 ± 3.5^{Aa}	88.5 ± 2.85^{Aa}	68.5 ± 6.1^{Ba}
Roughness	7 nm	0.2 ± 0.1^{Ba}	0.2 ± 0.1^{Ba}	0.6 ± 0.1^{Aa}
	12 nm	0.2 ± 0.1^{Ba}	0.3 ± 0.1^{Ba}	0.6 ± 0.1^{Aa}
	16 nm	0.2 ± 0.1^{Ba}	0.2 ± 0.1^{Ba}	0.6 ± 0.2^{Aa}

In each row, distinct capital letters indicate significant difference among the ageing condition while distinct lowercase letters in each column, indicate significant difference among filler size groups ($\alpha = 0.05$).

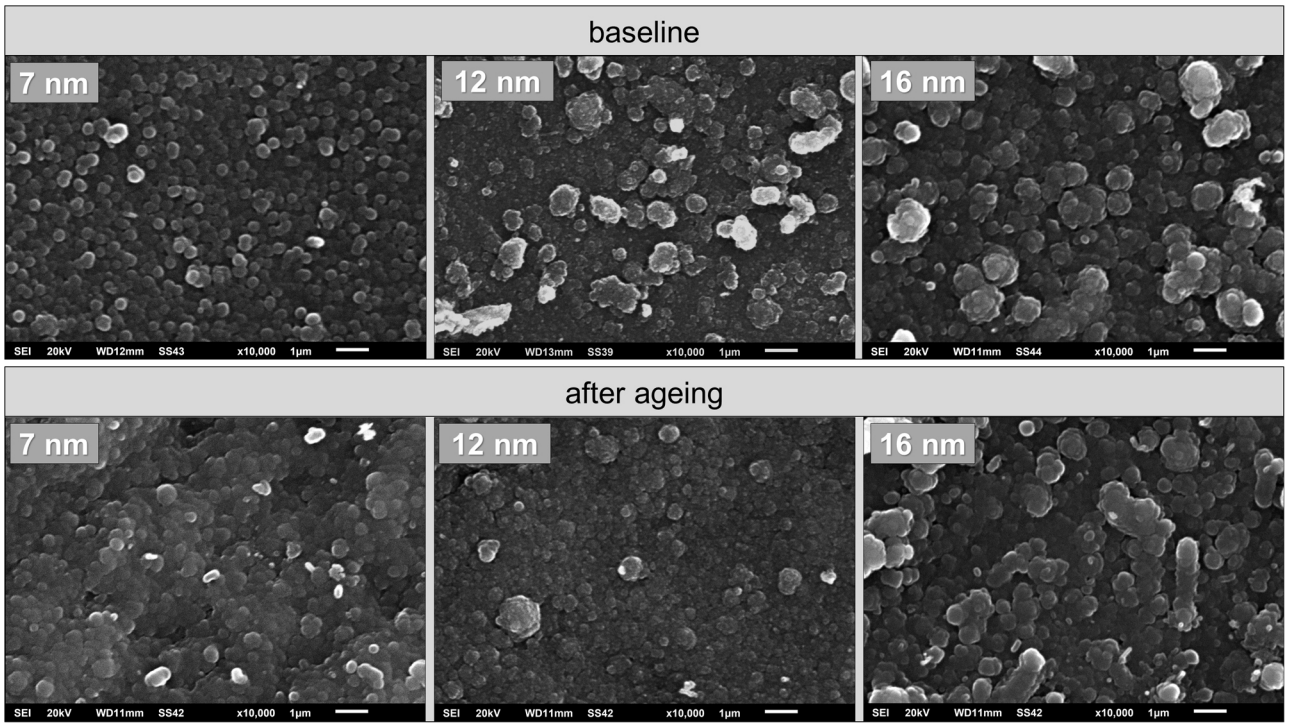

Fig. 2. Representative Scanning electron microscopy (SEM) analysis at ×10,000 magnification of each group at the baseline and after ageing (after water storage for 90 days and after 20,000 cycles of toothbrushing).

were those with the highest percentage of organic components, and therefore less percentage of inorganic content. However, it should also be noted that they studied composites with barium and zinc-glass fillers that were much larger than the fumed silica nanofillers used in the current study.

It was observed that the color stability was improved with a smaller filler size. The same fillers used in this study were tested previously [9], when different model composites were made with equivalent filler mass (45.5 wt%), and it was observed that water storage increased the color difference for all groups, but with a tendency for better color stability with the smaller filler size. This was related to the greater homogeneity of the distribution of the smaller fillers into the polymeric matrix when compared with the larger ones, and also by the degradation of the silane coupling agents [7]. The fillers used in the current study consist of hydrophobic fumed silica after being treated with hexamethyldisilazane (HDMS) in Aerosil® R 812 (7 nm), with an octylsilane in Aerosil® R 805 (12 nm) and with dimethyldichlorosilane (DDS) in Aerosil® R 972 (16 nm). The specifications about concentration of the employed silane coupling agents, as well as the silanization process, are not described by the manufacturer. The presence of an alkyl chloride in DDS may lead to a higher water uptake rate due to the hydrogen bonding interaction with a water molecule [25]. This is important to be considered since the silane layer may also influence the final optical properties. In the case of nanostructured resin-based composites, the silane phase plays an even more important role in the material properties, since the nanoscale fillers have an extremely high surface area-to-volume ratio and require a higher degree of silanization than larger fillers [26].

Translucency is one of the most important optical properties with respect to esthetics in dental restorations, since the translucency and opacity are indicators of the quality and quantity of reflected light. Translucency results from the relationship between the refractive indices of the filler and matrix materials. The greater the difference in refractive index, the higher the opacity, and the lower the translucency [8]. In this study it was observed that the lower the inorganic content fraction in the composite, the higher was the TP. The main component of a dental composite that significantly affects the translucency is its inorganic content [5,27,28] and it is known that the quantity, size and shape of filler affects light scattering in resin-based composites [29]. Considering the difference in refractive indices, the amount of the inorganic content is also crucial in this optical parameter. If filler size is far below the wavelength of visible light, it will not scatter or absorb the light, resulting in the human eye's inability to detect the effect of the fillers. In theory, nanostructured resin-based composites can produce superior translucency and may deliver optimal aesthetics [30]. It has been reported that the translucency parameter is altered after water storage due to the increased surface energy and the interposition of a thin layer within two media with distinct refractive indices. The composites absorb water in the matrix-filler interface and undergo hydrolytic degradation, altering the pattern of light diffusion [31] and this explains the similar translucency parameter results through ageing among the materials tested

Gloss is a visual attribute of the geometric distribution of the reflected light from a surface and is an indicator of surface smoothness. The higher the gloss, the higher is the surface luster, and it is known that higher gloss can reduce the color difference effect, since the reflected light is predominant rather than the light reflected from the underlying composite material [32]. It was reported that light reflectivity is related to the filler size and to filler-matrix homogeneity. The lower the filler-matrix homogeneity, the lower the light reflectivity [31]. In the present study, the materials did not differ with respect to gloss, likely due to the small size of the particles which ensured that scattering of light from the very smooth surface was minimal. However, the mechanical wear that caused surface abrasion during toothbrushing decreased the gloss for all groups, and this is due to changes in the surface topography with polymeric matrix abrasion and loss of fillers. The

decrease in gloss due to abrasion has been reported in other studies that showed a negative correlation with roughness [9,13,33,34].

The mechanical wear of the composites by surface abrasion takes place through a gradual removal of the polymeric matrix. This leaves the fillers unsupported and susceptible to exfoliation [35]. The abrasion resistance attributed to resin-based composites with smaller filler sizes could be related to their inter-filler spacing, which increases as filler size increases. A decrease in this spacing was the key for improving the wear-resistance of resin-based composites [36]. Fillers in close proximity protect the softer polymeric matrix from abrasives and produce a larger contact area between fillers and the antagonist, thus reducing wear [37]. The second research hypothesis of this study was accepted. The resin-based composites with different filler content but equal filler surface area presented similar surface properties through ageing. No significant differences were observed among the groups regarding gloss and roughness. The water storage alone did not lead to any significant difference, but toothbrushing did decrease gloss and increase roughness as expected. These similar results shown by the different filler content could be explained by the equivalent distribution of surface energy, when equalizing the surface area of the fillers.

5. Conclusion

Considering the limitations of the present study it can be concluded that:

- CIELAB individual parameters, CIELAB color difference, and translucency parameter were not dependent of the surface area of the filler, but were dependent upon the amount and coupling treatment of the filler;
- Gloss and roughness were constant for all groups, before and after the ageing procedures. The materials with different filler amounts and coupling treatment, but with equivalent surface areas, did not show significant differences in the surface properties.

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