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Influence of photoinitiator system and nanofiller size on the optical properties and cure efficiency of model composites

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ABSTRACT

Objective. To establish the relationship between photoinitiator system and nanofiller size on the optical properties and cure efficiency of model composites.

Methods. Model composites based on BisGMA/TEGDMA (60:40 mol%) were loaded with 40 wt% of 7 nm or 16 nm-sized filler particles. One of the following photoinitiator systems was added: camphorquinone (CQ) associated with an amine (EDMAB), monoacylphosphine oxide (TPO), or bysacylphosphine oxide (BAPO). The optical properties of disk-shaped specimens were measured 24 h after curing and repeated after storage in water for 90 days and coffee for 15 days. A large spectrum LED unit (Bluephase G2, Ivoclar Vivadent) was used for photoactivation. CIE $L^*a^*b^*$ parameters, color difference (ΔE), and translucency parameter (TP) were calculated. Knoop hardness readings were taken at top and bottom composite surfaces. Cure efficiency was determined by bottom/top hardness ratio. Data were statistically analyzed at $\alpha = 0.05$ significance level.

Results. Composites formulated with 16 nm particles had higher CIE L^* than those with 7 nm particles in all storage conditions. BAPO-based composites generally had lower CIE a^* than the other composites. The group TPO + 16 nm before storage and all groups with 16 nm-sized particles after storage had lower CIE b^* (i.e. lower degree of yellowing) than the other groups. TPO-based materials had higher color stability. The cure efficiency was not significantly affected by photoinitiator system or particle size. CQ + 7 nm had the lowest and BAPO + 16 nm the highest hardness values.

Significance. Combination of photoinitiator system and filler particle size might affect the optical properties of composites, with low influence on cure efficiency.

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1. Introduction

The photoinitiator system in dental composites is a group of molecules capable of absorbing light and as a result, directly or indirectly, giving rise to reactive species that can initiate polymerization. Photoinitiator molecules usually have in their structure a carbonyl group, which presents one electron capable of being transformed in anti-bonding orbital when exposed to light at appropriate wavelengths [1]. Association of camphorquinone (CQ) with a tertiary amine has been largely used as the photoinitiator system since the introduction of visible-light activated dental composites. CQ is a solid chromophore, meaning that the molecular structure includes a chromatic group that makes the material photoactive, in turn bringing a strong yellow color for the material. For esthetic reasons, the use of photoinitiator systems alternative to CQ/amine has been suggested [2].

The use of less yellow photoinitiators such as the phosphine oxide derivatives monoacylphosphine oxide (MAPO, also known as TPO) or bysacylphosphine oxide (BAPO) could minimize problems related to the color instability of CQ-based materials. TPO and BAPO absorb light at shorter wavelengths than CQ and, as a consequence, present a very pale yellow color or no color at all. BAPO and TPO are Norrish Type 1 photoinitiators, which means that they generate free-radicals by a photocleavage process that does not require a co-initiator. Type 2 photoinitiators, such as CQ, need a co-initiator molecule to effectively generate free-radicals, which are formed from displacement of hydrogen from the photoinitiator [2]. Amines are known to generate by-products during photoreaction, which tend to cause discoloration from yellow to brown, depending on the type and fraction of amine in the system [3,4]. In addition, there is a potential cytotoxicity of unreacted CQ and amine molecules eluted from the composite [5,6].

Previous studies have demonstrated the polymerization efficiency of TPO and BAPO [7–10]. These photonitiators require a modification of the existing dental lights to extend the emission profile beyond blue light wavelengths for better curing. To accommodate that, several companies have developed new light-emitting-diode (LED) curing units that are capable of activating resin composites containing other photoinitiators, which highlights the commercial potential of these alternative systems. TPO and BAPO both have maximum absorption peaks (λ_{max}) close to UV radiation, although their absorption profile extends toward the visible light region of the electromagnetic spectrum [8].

Despite the several benefits derived from photoreaction, the polymerization of composites is limited to the depth of light penetration. In composites, high filler loading causes light to be absorbed and scattered, and thus attenuated as it passes through the material. Polymerization is usually far more efficient on the surface close to the light source, and that efficiency decreases at deeper portions. This creates a gradient of polymerization within the material, and may result in undercured layers at the bottom areas [11]. It is known that the quantity, size, and shape of particles all affect the scattering of light through the composites [12]. A previous study reported that use of larger nanoparticles increased lightness and reduced the yellowing effect of composites, whereas materials with smaller particles tended to have increased color stability [13]. However, to the best of our knowledge, no data is available about the relationship between alternative photoinitiator systems and particle size in nanostructured composites and their influence on optical properties.

The aim of this study was to establish a relationship between photoinitiator system and nanoparticle size on the optical properties and cure efficiency of model dental composites. The hypotheses of this study were: (i) composites formulated with CQ would present higher yellowing effect and higher color difference during storage than composites with BAPO or TPO; (ii) composites formulated with higher nanoparticle size would have lower yellowing effect and higher lightness than composites with lower nanoparticles; (iii) composites formulated with TPO and BAPO would present higher curing efficiency than composites formulated with CQ.

2. Materials and methods

2.1. Formulation of the model composites

Experimental composites were formulated by a 60:40 mol% mixture of BisGMA and TEGDMA (Esstech, Essington, PA, USA). Composites were prepared by incorporating 40 wt% of nanoparticles with either 7 nm (Aerosil® R 812, Evonik, Germany) or 16 nm (Aerosil® R 972) in average size. Fillers consist in hydrophobic fumed silica particles treated with hexamethyldisilazane (Aerosil® R 812) or dimethyldichlorosilane (Aerosil® R 972). Composites with three different photoinitiator systems added at 1 mol% were tested: CQ associated with ethyl 4-dimethylaminobenzoate (EDMAB), TPO, or BAPO, all from Sigma–Aldrich (Chemie, Steinheim, Germany). The photoinitiators were diluted in TEGDMA and then BisGMA was added. Fillers were gradually incorporated by hand-mixing and then the materials were mechanically mixed using a centrifugal mixer (SpeedMixer DAC150; FlackTek, Landrum, SC, USA) to produce a homogeneous paste. Six composites were formulated based on distinct filler size – photoinitiator system combinations.

Disk-shaped specimens were made in a circular steel mold (8 mm in diameter, 2 mm in thickness). After composite insertion, the top surface was covered with a Mylar strip and made flat by pressure with a glass slide. For each group, 12 specimens were obtained: six were used for optical properties analysis, and the other six for cure efficiency analysis. The specimens were light cured from the top surfaces for 40 s with a large spectrum LED curing unit (Bluephase G2; Ivoclar Vivadent, Schaan, Liechtenstein) with irradiance of 1200 mW/cm^2. All specimens were mechanically polished in both surfaces in a grinding/polishing machine (Buehler, Lake Bluff, IL, USA) with a sequence of 2000- and 4000-grit SiC papers under continuous water cooling.

2.2. Optical properties analyses

The optical properties were determined according to the CIELAB parameters in the reflectance mode, with the specular component included (SCI) mode, over a zero calibrating box

(CIE $L^*=0.0$, $a^*=0.0$, and $b^*=0.0$), a white background (CIE $L^*=93.2$, $a^*=-0.3$, and $b^*=1.6$), and a black background (CIE $L^*=0.5$, $a^*=0.7$, and $b^*=-0.6$) using a spectrophotometer (CM-2600d, Konica Minolta, Ramsey, NJ, USA) with a circular, 6 mm diameter aperture. The SCI mode is the recommended operational mode of spectrophotometer with an integrate sphere for color measurement of resin composites. The specular component is the reflected light from the surface such that the angle of reflection equals the angle of incidence [14]. 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.

CIE L^*, a^*, and b^* values were automatically calculated by the equipment. The CIE L^* is the lightness, with 100 for white and 0 for black. The axes CIE a^* and CIE b^* are the red-green and yellow-blue chromatic coordinates respectively. A positive CIE a^* or CIE b^* value represents a red or yellow shade, and a negative CIE a^* or CIE b^*, represents green or blue respectively. Measurements were obtained after dry and dark storage at 37 °C for 24 h after polymerization (baseline) and after immersion in distilled water at 37 °C for 90 days. After water storage, the specimens were immersed in coffee solution for 15 days at 37 °C in order to subject the specimens to external staining. The solution was made with 3.6 g of coffee powder (Melitta Extra Forte, Melitta do Brazil, São Paulo, Brazil) dissolved in 300 mL of boiling distilled water. After 10 min of stirring, the solution was filtered through a filter paper (Melitta do Brazil, São Paulo, Brazil) [15]. The CIELAB color difference (ΔE) was calculated from the average of $L^*a^*b^*$ values of each specimen using the formula [16]:

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

where ΔL^*, Δa^* and Δb^* are the mathematical differences between $L^*a^*b^*$ of the different evaluated periods and baseline. The translucency parameter (TP) was calculated using the formula [17]:

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

where the subscript "w" refers to CIELAB values for each specimen on the white background and the subscript "b" refers to values for specimen on the black background.

2.3. Cure efficiency analysis

Twenty-four hours after dry storage in the dark, hardness readings were taken using a microhardness tester (Micromet 5104; Buehler, USA) under a load of 25 N for 15 s. Readings were taken at five locations on both top and bottom composite surfaces. The Knoop hardness number (KHN, kgf/mm^2) for each surface was calculated as the average of five readings. To check the cure efficiency, the ratio of bottom and top hardness values was calculated. The closer to one is the ratio value the more efficient is the curing process. KHN readings were taken again at top surfaces after seven days of storage in absolute ethanol (Synth, Diadema, SP, Brazil).

2.4. Statistical analysis

Statistical analysis was conducted using SigmaSTAT® 3.5 software (Systat Software, San Jose, CA, USA). Data for CIELAB individual parameters, ΔE, TP, and top KHN as a function of ethanol storage were submitted to two-way repeated measures analysis of variance (one factor repetition), with photoinitiator/filler size combination and storage condition as factors. KHN ratio data were analyzed using one-way analysis of variance. Heteroscedastic data sets were rank-transformed before statistical analysis. All pairwise multiple comparisons procedures were performed using the Student–Newman–Keuls' method ($\alpha = 0.05$).

3. Results

3.1. CIELAB parameters

Values of CIE L^* (lightness), a^* (green and red coordinates), and b^* (blue and yellow coordinates) before and after water and coffee storage are shown in Fig. 1. For CIE L^*, the factors 'photoinitiator/filler size combination' ($p = 0.001$) and 'storage condition' ($p < 0.001$) as well as the interaction between factors ($p = 0.04$) were significant. In all storage conditions, composites formulated with 16 nm particles showed significantly higher CIE L^* than those with 7 nm particles for all photoinitiator systems. No significant differences in CIE L^* were observed between photoinitiators with same filler size in any storage condition. For each photoinitiator/filler size combination, storage in water significantly increased CIE L^*, whereas storage in coffee significantly reduced CIE L^* for all groups but CQ + 16 nm and BAPO + 16 nm.

For CIE a^*, the factors 'photoinitiator/filler size combination' and 'storage condition' were both significant ($p < 0.001$), whereas the interaction between factors was not significant ($p = 0.081$). Composites formulated with BAPO showed significantly lower CIE a^* than the other composites, except after storage in coffee. TPO-based materials generally had higher CIE a^* than the other composites in the baseline analysis, but this difference was not observed after storage. No significant differences in CIE a^* were observed between photoinitiators with same filler size in any storage condition. The filler size had no significant impact in CIE a^* values. For each photoinitiator/filler size combination, storage in water and then in coffee significantly increased CIE a^*.

For CIE b^*, both statistical factors and their interaction were significant ($p < 0.001$). In the baseline analysis, the group TPO + 16 nm was significantly less yellow (lower CIE b^*) than the other groups. After storage in water and then coffee, all composites formulated with 16 nm particles had significantly lower CIE b^* than composites with 7 nm particles. For each photoinitiator/filler size combination, storage in water significantly decreased the CIE b^* values, which receded slightly after storage in coffee for all groups except TPO + 16 nm.

3.2. Color difference (ΔE) and TP

Results for ΔE are shown in Fig. 2. Both statistical factors were significant ($p < 0.001$), whereas their interaction was not significant ($p = 0.634$). After water storage, TPO-based composites presented significantly lower ΔE than the other materials, and there was no significant difference between CQ and BAPO. After the additional 15 days of coffee storage, ΔE values of

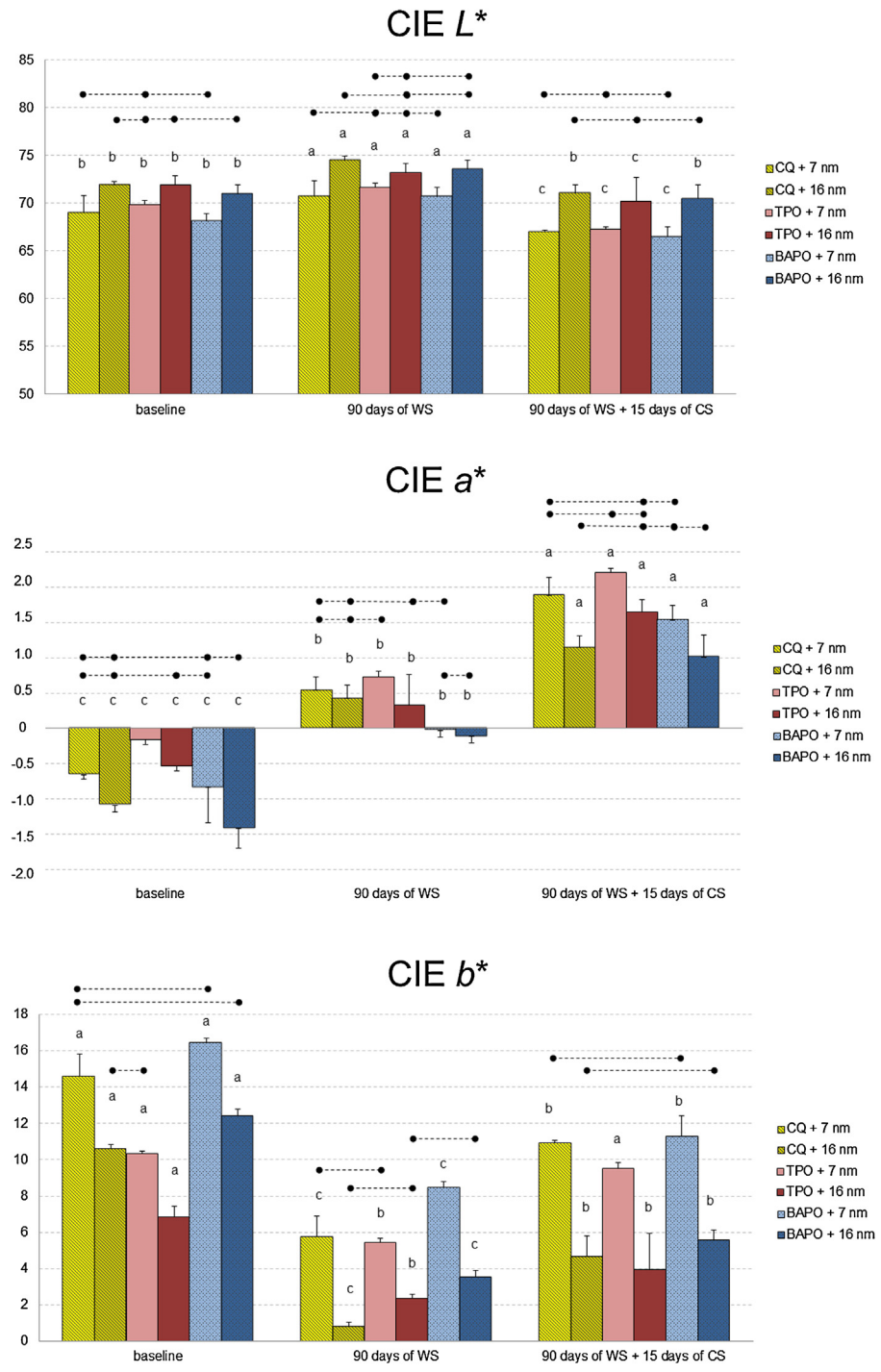

Fig. 1 – CIE L^*, CIE a^*, and CIE b^* at baseline and after storage in water (WS) and coffee (CS). Bars are means + standard deviations ($n = 6$). Distinct letters indicate statistical differences between storage conditions for each photoinitiator/filler size combination. Statistically similar groups in each storage condition are indicated by connected dots above bars.

all groups were significantly reduced, but the results for TPO-based materials were still significantly lower than the other photoinitiators. After storage in coffee, CQ- and BAPO-based composites with 7 nm particles had significantly lower ΔE values than composites with 16 nm particles. TP results are presented in Fig. 3. CQ + 7 nm presented the highest values, irrespective of the storage condition, while the other groups had no significant differences. Water storage significantly decreased TP values of composites with 16 nm-sized particles, while storage in coffee significantly decreased TP of TPO + 7 nm, TPO + 16 nm and BAPO + 7 nm groups (Fig. 3).

3.3. *Cure efficiency*

Results of the cure efficiency analysis are shown in Table 1. For CQ, composites with 16 nm particles showed significantly

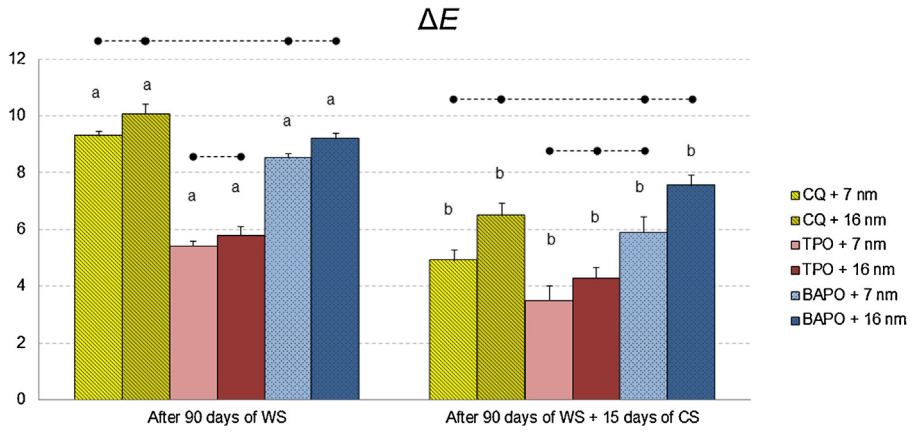

Fig. 2 – Results for ΔE after storage in water (WS) and coffee (CS) compared with baseline. Bars are means + standard deviations (n = 6). Distinct letters indicate statistical differences between storage conditions for each photoinitiator/filler size combination. Statistically similar groups in each storage condition are indicated by connected dots above bars.

higher top and bottom hardness than composites with 7 nm particles, while the other photoinitiators had no significant differences. The bottom/top KHN ratios were similar among groups. After ethanol storage all composites showed significantly lower top hardness, with CQ + 7 nm composite still showing the lowest hardness results among photoinitiator/filler size groups.

4. Discussion

The first hypothesis of this study was rejected because composites formulated with BAPO and CQ had similar degree of yellowing. After 90 days of water storage, the specimens of all groups showed a decrease in the CIE b^* and increase in CIE a^* axes. This could be related to leaching of unreacted monomers and photoinitiators by water dissolution [2]. The increased CIE b^* values in all groups after storage in coffee might be associated with the surface staining caused by pigments in the solution [15]. The color change resulting from contact with the coffee solution originates, in most cases, from extrinsic staining, but internal material discoloration may also occur. Pigmentation caused by coffee might occur by surface adsorption of dark pigments and absorption of pigments at the subsurface layer [18].

At baseline color evaluation, BAPO showed the highest yellowing effect. Similar results were also found by Arikawa et al. [19], who observed that BAPO presented degree of yellowing close to CQ. Although the λ_{max} for BAPO lies near 370 nm, its absorption activity extends toward the visible region of the electromagnetic spectrum, above 400 nm. This factor makes the perception and absorption in the yellow region more evident, affecting both the color stability of composites and their final esthetics [8]. By comparison, TPO presented the lowest degree of yellowing irrespective of the evaluation period, particularly when 16 nm-sized particles were used. This finding is associated with the low color saturation and high reactivity of TPO [2,20].

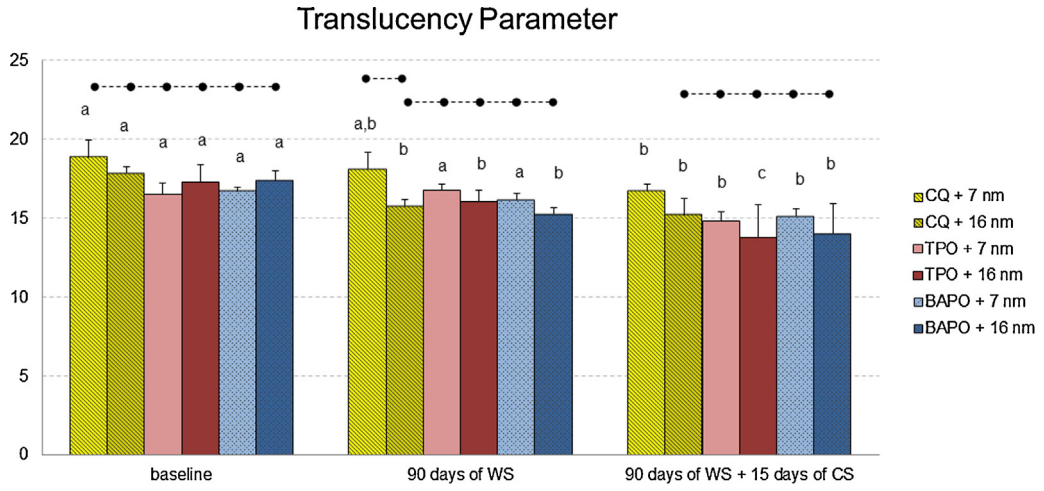

Fig. 3 – Results for translucency parameter after storage in water (WS) and coffee (CS). Bars are means + standard deviations (n = 6). Distinct letters indicate statistical differences between storage conditions for each photoinitiator/filler size combination. Statistically similar groups in each storage condition are indicated by connected dots above bars.

Table 1 – Results of the cure efficiency analysis ($n = 6$). Values are Knoop hardness number (KHN, kgf/mm^2) means ± standard deviations.

Photoinitiator/filler size	Top hardness	Bottom hardness	Bottom/top ratio	Top KHN as a function of ethanol storage	
				Before	After
CQ + 7 nm	28.5 ± 0.8A,d	21.5 ± 3.2B,c	0.75 ± 0.10a	28.5 ± 0.8A,d	14.9 ± 1.3B,c
CQ + 16 nm	33.7 ± 0.7A,bc	24.0 ± 0.1B,b	0.71 ± 0.03a	33.7 ± 0.7A,bc	18.5 ± 1.2B,b
TPO + 7 nm	30.7 ± 3.4A,cd	24.6 ± 3.4B,b	0.80 ± 0.03a	30.7 ± 3.4A,cd	18.0 ± 0.6B,b
TPO + 16 nm	33.4 ± 1.2A,c	23.1 ± 2.6B,b	0.69 ± 0.06a	33.4 ± 1.2A,c	19.3 ± 1.7B,b
BAPO + 7 nm	36.5 ± 1.4A,ab	28.0 ± 3.2B,a	0.77 ± 0.12a	36.5 ± 1.4A,ab	21.9 ± 1.7B,b
BAPO + 16 nm	40.8 ± 1.1A,a	32.3 ± 1.9B,a	0.79 ± 0.06a	40.8 ± 1.1A,a	28.2 ± 2.0B,a

In the first two columns, distinct capital letters in each row indicate significant differences between top and bottom hardness, while distinct lowercase letters in each column indicate significant differences between photoinitiator/filler size groups. No significant differences in bottom/top ratios were observed. In the last two columns, distinct capital letters in each row indicate significant differences before and after ethanol storage, while distinct lowercase letters in each column indicate significant differences between photoinitiator/filler size groups ($\alpha = 0.05$).

Regarding filler size and its influence on optical properties of composites, it was observed that composites with 16 nm particles generally had higher lightness and were less yellow than composites with 7 nm particles. Thus, the second hypothesis was accepted. A recent systematic review has shown that nanofilled composites usually have similar surface roughness and gloss than submicron and microhybrid composites even after surface challenges [21]. It is interesting to note, however, that composites with 16 nm-sized particles generally presented lower color stability than 7 nm-sized particles. The color stability of dental composites is influenced by extrinsic factors, such as the absorption of coloring solutions (e.g. coffee) or by intrinsic factors that leads to chemical changes in the entire restoration. Therefore, if the staining is not in the superficial layers it is not possible to be removed by polishing procedures. Intrinsic color changes might be caused by the photoinitiator system [22]. Changes in CIE L^*, a^*, and b^* parameters during storage may also be explained by hydrolysis reactions. Color stability might be related to water sorption and solubility, which cause polymer matrices to swell and reduce the frictional forces between polymer chains [23]. Since water has a much different refractive index than the polymer network and filler particles, light transmission could be impaired by refraction at the polymer-filler-water interfaces. Ultimately, that might leads to increased light scattering and changes in the perception of color [24].

ΔE values lower than 1.0 are considered as not appreciable by the human eye as well as ΔE values between 1.0 and 3.3 are appreciable by skilled operators, but still in a clinically acceptable range. On the other hand ΔE values greater than 3.3 are perceivable even by untrained observers and, for this reason, are considered as not clinically acceptable [25]. The ΔE values in this study ranged between 3.5 and 10.1, indicating that all experimental groups presented unacceptable color changes during storage. A potential explanation for this result is that the inorganic loading of the model composites tested here are much lower than commercial composites. Therefore, the color changes occurring due to leaching and/or degradation of the resin matrix and photoinitiator components are more evident.

Translucency and opacity are fundamental factors in achieving esthetic restorations with composites, since they are indicators of the quality and quantity of reflected light [26]. The main component of a dental composite that significantly affects its translucency is the inorganic content [27]. It is known that the quantity, size, and shape of particles all affect the light scattering in dental composites [12]. When particle size is below the wavelength of visible light, it is considered that it could not scatter that particular wavelength. If particle size is far below the wavelength of light, it would not scatter or absorb the light, resulting in inability of the human eye to visualize the particles [28]. Both particle sizes used here are far below the wavelength of light, so that was unlikely a factor affecting the results. It should not be ignored, however, that filler agglomeration could also interfere with the optical properties. Another factor that affects translucency is the mismatch in refractive indices between filler and matrix. The filler increases light scattering at the resin-filler interfaces, tending to produce opaque materials. The opacity of the composite is raised as the refractive index difference between filler and resin matrix increases [28]. As the degree of C=C conversion increases, the mismatch between refractive indices decreases, which means that composites that achieved lower conversion are likely to have more light scattering [29].

It has been reported that the TP is altered after immersion in water at 37 °C for 24 h due to the increased surface energy and interposition of two media with distinct refractive indices [30]. Composites may absorb water at the matrix-particle interface and undergo hydrolytic degradation, altering the pattern of light diffusion [30]. Results of TP in this study showed that the group CQ + 7 nm presented the highest TP, and that some groups had reduced TP after storage. These results could be related to different polymerization extents and difference in refractive index when monomers are converted into polymer. The lower the degree of C=C conversion the higher might be difference between the refractive indices between filler particles and resin matrix [27].

Hardness was significantly higher at the top than bottom composite surfaces in all groups. It is known that light achieves the top surface very easily, with minimum attenuation, and consequently more efficiently reaching and exciting the photoinitiator molecules [31]. Softer bottom surfaces are a result of reduced irradiance as light travels through the material, i.e. the quantity of photons that reaches the bottom surface is not the same that reaches the top surface [32]. Usually, larger particles generate composites with higher hardness due to the higher resistance of surface to indention

[33]. However, in this study, larger particles led to higher hardness only for materials with CQ-amine, probably due to lower polymerization efficiency of this binary system. BAPO-based composites were generally harder at top and bottom surfaces than CQ and TPO-based materials. BAPO is a very efficient molecule that presents four potentially active radicals for each molecule [8]. As a result, more active centers for radical formation and chain extension are formed, also favoring crosslinking, which makes the polymer less susceptible to softening.

In this study, hardness values of TPO-based composites were similar to CQ-based materials. Using the differential scanning calorimetry, Schneider et al. [20] evaluated the kinetics of polymerization of model resin composites containing different photoinitiator systems. The authors observed that TPO was capable of promoting higher C=C conversion than CQ using a halogen curing unit. However, a recent study diverges as regards the feasibility of polymerization of materials formulated with TPO, since its absorption in wavelengths lower than CQ may cause lower values of conversion in deeper composite portions [10]. A possible reduction in depth of cure, however, is irrelevant when composite increments no thicker than 3 mm are used [20].

After evaluating the hardness of dry surfaces, all groups were stored for seven days in absolute ethanol for subsequent measurement. The results were that all groups showed a decrease in KHN values, as expected. Due to the large amount of [–OH] terminations present in ethanol, higher absorption occurs by the polar portion of the matrix, causing swelling. This dimensional change in the matrix causes stress at the matrix-silane-filler particle interfaces, resulting in degradation of the bonds. As a consequence, inorganic particles may detach from the surface, causing an increase in surface roughness and contributing to make the surfaces softer [33]. The results of hardness test after ethanol storage were basically the same as before storage as regards the influence of photoinitiator system and filler particle size.

5. Conclusions

Combination of photoinitiator system and filler particle size might affect the optical properties of dental resin composites, with minor influence on cure efficiency. Composites formulated with 16 nm-sized particles had higher lightness and were generally less yellow than composites with 7 nm-sized particles. The color stability of TPO-based materials was higher compared with the other photoinitiator systems.

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