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Photoinitiator concentration and modulated photoactivation: influence on polymerization characteristics of experimental composites

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Abstract

This study determined the influence of photoinitiator concentration on polymerization characteristics of experimental composites photoactivated by different methods. Composites based on BisGMA/TEGDMA and 65% of filler were prepared with the concentration of camphorquinone/amine C1-0.5%, C2-1%, C3-1.5%, and photocured using 4 methods: High-intensity (HI), Low-intensity (LI), Soft-start (SS) and Pulse-delay (PD). Were determined the degree of conversion (DC), depth of cure (DCure) and crosslink density (CLD). Data were submitted to ANOVA and Tukey's test ($p < 0.05$). DC and DCure revealed that there were no differences among the photoactivation methods. C3 and C2 showed higher DC than C1. The CLD evaluation revealed considerable differences among the photoactivation methods. Photoinitiator concentration is a determinant factor in the polymerization characteristics of composites. Composite with low photoinitiator concentration show decreased DC and DCure, when compared with the composites with higher concentrations. Photoactivation methods had no effect on the DC and DCure. However, photoactivation methods showed differences when CLD was tested for composites with higher concentration of photoinitiators.

Keywords: Resin composites; Photoactivation; Photoinitiator; Camphorquinone; Pulse delay; Soft-start

Background

Increasing the conversion of double bonds during the photopolymerization is critical for the optimization of mechanical properties [1,2], biocompatibility [3,4] and color stability [5] of light-activated dental resins. Photopolymerization implies both in the increase of molecular weight by monomer to polymer conversion, as well as cross-linking of developing or preexisting macromolecules [6].

In dental composites, camphorquinone (CQ) is the most employed photosensitizer or photoinitiator. After light absorption between 400 and 500 nm (maximum at 470 nm) CQ is promoted to an excited triplet state that interacts with an electron- or proton-donor molecule, like a tertiary amine, to generate free radicals [7,8].

Despite of its efficiency, CQ is inherently yellow, which causes problems in color matching to natural teeth. In addition, there are also limits on the amount of amine

used by the tendency to internal discoloration of the resin. In addition to these problems, a high quantity of initiator also induces quick and high generation of free radicals, what could result in reduction of the reaction ability of the monomers due to the surrounding polymer network, and polymers with relatively lower molecular weight are formed. Also, most of the created radicals rapidly disappeared without being used in the polymerization because of their short period of life. This, in turn, places practical limits on the concentration of photoinitiators, and consequently, limits the degree of polymerization and depth of cure that can be attained [7-11].

Conversely, if the concentration of photoinitiators were kept too low, photocurable composite materials could be under-cured. If inadequate levels of conversion are achieved in the polymerization, mechanical properties and wear performance can be compromised [1], amount of leachable residual monomer increase and color stability may decline [4,5,7]. However, if conversion is maximized to reduce these difficulties, then problems inherent polymerization shrinkage of the composite become more critical [1].

Photoinitiator concentration and the light intensity can also influence polymerization rate [8,10,11]. The polymerization rate can regulate the cross-linking density, which is very important because a reduction in the effective cross-linking density of a cured resin will lead to a decrease in its mechanical strength, solvent resistance, and glass transition temperature [12].

Studies on alternative photoactivation methods have shown the beneficial effects of a modulated polymerization [13-15]. A slow curing allows a slow development of the composite stiffness and leads to better flow, what can reduce the shrinkage stress [13,14]. Previous studies [15,16] have shown that the marginal adaptation of resin composites can be improved by light curing with low power density. Conversely, there are studies that claim that these benefits are consequences of lower degree of conversion [17] and that high intensity is necessary to achieve deep and complete polymerization of the material [13].

Because of this, modulated photoactivation methods as soft-start and pulse delay have been proposed [13-16]. Yoshikawa *et al.* [18] observed that soft-start photoactivation can lead to better marginal adaptation of composite restorations. The pulse delay photoactivation method, which is a combination of low energy density followed by a lag period before a final high power density irradiation, can also decrease the intensity of polymerization stress [13,14]. It was hypothesized that PD technique resulted in a polymer structure with lower cross-link density and that slow start polymerization techniques are associated with relatively few centers of polymer growth which may favor the formation of a more linear polymer structure with relatively few cross-links [19,20]. On the other hand, a rapid standard continuous cure will initiate a multitude of growth centers and a polymer with a higher crosslink density.

Considering that the aim of this study was to determine the influence of photoinitiator concentration on polymerization characteristics of experimental composites photoactivated by different methods. The first tested hypothesis was higher concentration of photoinitiator can increase degree of conversion, surface hardness, depth of cure and cross-link density. The second testes hypothesis was the photoactivation method does not affect the polymerization characteristics as degree of conversion, surface hardness and depth of cure, but the cross-link density will be higher in composites photoactivated using continuous high intensity method.

Methods

Formulation of experimental composites

Monomer mixtures consisting of 65 wt% of BisGMA (2,2-bis[4-(2-hydroxy-3-methacryloxypropoxy)phenyl]propane) and 35 wt% of TEGDMA (triethylene glycol dimethacrylate) were prepared. The light-curing initiator system selected was camphorquinone (CQ), as photoinitiator, and dimethyl aminoethyl methacrylate (DMAEMA), as co-initiator, (proportion 1:1 by weight). The light-curing initiator system (CQ/DMAEMA) was thoroughly dissolved in the monomer matrix in the following concentrations: 0.5 wt% (C1), 1.0 wt% (C2) e 1.5 wt% (C3). Also, the inhibitor BHT (butylated hydroxytoluene) was added to the organic matrix in a concentration of 0.1 wt% to avoid spontaneous polymerization of the monomers. The organic matrix was reinforced with silanized barium aluminum silicate glass fillers (BaAlSi - average size: 0.5 μm) and silica (SiO_2 - average size: 0.04 μm). The fillers were added incrementally and mixed homogeneously up to 65 wt%. Considering this filler content, 80 wt% were BaAlSi and 20 wt% were SiO_2 . The manipulation of the experimental composites was carried out under filtered orange light. The formulation of the experimental composites used in this study was selected based on the studies of Park *et al.* [7], Atai & Watts [21] e Moin Jan C *et al.* [22]. All reagents were from Sigma-Aldrich Inc, St Louis, MO, USA.

Degree of conversion

Degree of conversion of the experimental composites was measured using FTIR spectroscopy (Bomem, model MB-102, Quebec- Canada) at a resolution of 4 cm^{-1} and 32 scans in the range of 4000–300 cm^{-1} . In order to obtain the specimens ($n = 3$), the experimental composites (C1, C2 and C3) were placed in a circular brass mold 6 mm in diameter and 2 mm in height and covered with polyester strips. A glass slide was placed over the strips and excess material was extruded by pressure application. The glass slide was removed and the composite was irradiated from the top through the polyester strip using the different photoactivation methods (Table 1). Subsequent to photoactivation, the specimens were finely pulverized with a hard tissue-grinding machine (Marconi, model MA590, Piracicaba-SP, Brazil) and maintained in a dark room for 24 h. After, 10 mg of the ground powder were mixed with 100 mg of KBr powder salt. This mixture was placed into a pelleting device (Aldrich, Milwaukee, WI, USA) and then pressed in a hydraulic press (Carver Laboratory Press, model 3648, Wabash, St Morris, USA) with a load of 8 tons to obtain a pellet. This pellet was then placed into a holder attachment within the spectrophotometer (Bomem, model MB-102, Quebec-Canada) for analysis. The uncured

Table 1 Photoactivation methods used in this study

Photoactivation method*	Protocol (Irradiance and Exposure time)
Continuous high intensity (HI)	700 mW/cm^2 during 40 s
Continuous low intensity † (LI)	150 mW/cm^2 during 186 s
Soft start † (SS)	150 mW/cm^2 during 10 s + 700 mW/cm^2 during 38 s
Pulse delay † (PD)	150 mW/cm^2 during 10 s + 3 minutes light off + 700 mW/cm^2 during 38 s

*The radiant exposure was standardized in 28 J/cm^2 for all groups. The light curing unit used was XL2500 (3 M/ESPE Dental Products, St. Paul, MN, USA).

†The reduction on irradiance was obtained using a standard separators calibrated to reduced the irradiance from 700 to 150 mW/cm^2 .

composite resin was analyzed using a metallic siliceous window. The absorbance peaks of the cured and uncured samples of C1, C2 and C3 were obtained. The percentage of unreacted carbon-carbon double bonds (% C = C) was determined from the ratio of absorbance intensities of aliphatic C = C (peak at 1638 cm^{-1}) against the internal reference aromatic C-C (peak at 1608 cm^{-1}) before and after curing of the specimen. The degree of conversion (DC%) was determined by subtracting the % C = C from 100%. Data were submitted to two-way ANOVA and means compared by Tukey's test at the 5% significance level.

Cross-link density

The degree of polymer cross-linking was assessed indirectly by measurements of the hardness before and after ethanol storage. In this evaluation, circular specimens (6 mm diameter \times 2 mm height) were obtained using the same circular brass mold used in the degree of conversion test. The composites (C1, C2, and C3) were irradiated using the photoactivation methods described in Table 1. Ten specimens were obtained for each group. Immediately after light polymerization, the specimens were dark stored in air at 37°C for 24 h. Next, the specimens were manually polished using 600, 1200 and 2000 grit sandpaper (Norton S.A., São Paulo, SP, Brazil) and subjected to hardness test using a Hardness Tester HMV 2000 (Shimadzu, Tokyo, Japan) at automatic procedure with a load of 50 g applied for 15 s. Baseline Knoop hardness values (KHN1) were recorded. After, specimens were stored in 3 ml of absolute ethanol solution at 37°C for 24 h and post-conditioning hardness (KHN2) was determined. Three readings were taken for each specimen and these were averaged to form a single value for that specimen. Percentage of hardness deterioration (%HD) was computed as follows: $\%HD = 100 - (KHN2 \times 100 / KHN1)$. Data were then subjected to ANOVA and Tukey's test at the 5% significance level.

Depth of cure

Specimens were prepared in a metallic brass containing a cavity with 3 mm in diameter and 5 mm in height, longitudinally split up in to equal parts, in order to facilitate specimen removal after polymerization. Each resin composite was inserted into the cavity in a single portion, exceeding a small amount from the margin of the cavity. The material was adapted by compression of polyester matrix under a glass slab, with static load of 1 kg, to remove the excessive material. After the glass slab removal the specimens were light cured according Table 1. Five specimens were prepared for each composite resin (C1, C2, and C3). After light curing, the specimens were removed from the metallic mold and dark stored at 37°C for 24 h on dry environment. The specimens were fixed using wax in a vertical position in an acrylic device containing 5 cavities (4 mm \times 6 mm \times 1.5 mm depth). Next, the specimens were ground and polished to the center, using 320, 600, 1200 and 2000 grit sandpaper (Norton S.A., São Paulo, SP, Brazil) on an automated polisher (APL-4, Arotec, Cotia, SP, Brazil). Knoop hardness values were measured across the section of the composite resin, using a Hardness Tester HMV 2000 (Shimadzu, Tokyo, Japan) at automatic procedure with a load of 50gf applied for 15 s. Three measurement positions (A, B, and C) were made, each with five indentations (from P1 to P5) from the top to the bottom of the specimen section, giving a total of

fifteen measurements for each specimen. The indentation layout is shown in Figure 1. The values obtained in micrometers were converted to Knoop Hardness Number (KHN), by indenter software. The results were submitted to three-way ANOVA and means compared by Tukey's test at the 5% significance level.

Results

Degree of conversion values and standard deviations for all photoactivation methods are listed in Table 2.

According to two-way ANOVA, the factor composite was significant and factor photoactivation method and the interaction photoactivation method x composite were not significant. Considering this, in conformity with Tukey's test results, Table 2 shows that the degree of conversion was not affected by the photoactivation method, regardless the photoinitiator concentration. The concentration of photoinitiators, however, showed a significant effect. The composite with 0.5 wt% of CQ/DMAEMA (C1) presented significant less conversion than the others (C2 and C3).

Indirect evaluation of cross-linking density, expressed in percentage of softening after storage in ethanol, and standard deviations for all photoactivation methods and types of composite are listed in Table 3. In this way, the higher the softening the lower the cross-linking density.

According to Table 3, cross-linking density was affected by the photoactivation method and the composite. C3 specimens polymerized with PD, SS and LI methods were significantly more susceptible to softening in ethanol than specimens cured with HI. No significant difference in cross-link density was observed between PD, SS and LI. For C2, specimens cured with LI showed the highest softening and those cured with HI the lowest softening, while specimens cured with PD and SS showed intermediate results. For C1, specimens cured with PD and LI provided significant less softening than the specimens cured with SS, while specimens cured with HI showed intermediate results.

Observing the photoactivation methods, when the specimens were photoactivated using SS and PD, there was no difference among the composite C1, C2 and C3: the softening was similar. For photoactivation with LI, C2 showed the highest softening, and it was significantly superior to the softening observed for C1 and C3. For photoactivation with HI, C3 showed significant lower softening than C2; C1 showed intermediated results, without significant difference from C2 and C3.

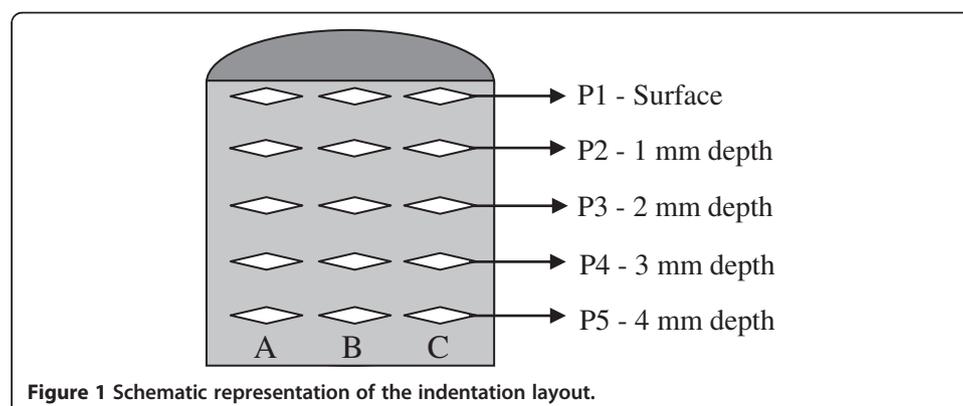


Figure 1 Schematic representation of the indentation layout.

Table 2 Results of degree of conversion (%) in relation to type of composite and photoactivation method, means (SD)

	C1	C2	C3	
HI	47.7 (1.30)	50.1 (0.60)	54.0 (3.84)	A
LI	47.6 (1.62)	50.8 (0.82)	49.3 (3.94)	A
SS	42.0 (3.41)	51.8 (3.45)	51.8 (3.74)	A
PD	47.6 (1.37)	51.3 (1.86)	51.5 (1.12)	A
	b	a	a	

Statistical differences are expressed by different capital letters in columns, and by different minuscule letters in rows ($p < 0.05$).

Depth of cure, expressed in millimeter (mm) and Knoop Hardness Number (KHN) at each depth and standard deviations for all photoactivation methods and types of composite are listed in Table 4.

In this study, the depth of cure was considered the depth at the KHN mean values had no statistical difference from those observed at the surface. The depth of cure was different for the experimental composites. The composite C1 showed depth of cure of 1 mm for all photoactivation methods while C2 showed depth of cure of 2 mm. C3 showed depth of cure of 2 mm when photoactivated with LI and PD and 3 mm when photoactivated with HI and SS. Considering the KHN obtained in each depth, the hardness of the composite with lower concentration of photoinitiators (C1) was significantly lowered than that observed for the other composites (C2 and C3) in almost all situations. In addition, it was observed that the composite C1 was completely unstiffened (not cured) at the depth of 4 mm, at this depth the KHN was 0.00 for all photoactivation methods.

The superficial hardness was not affected by the photoactivation methods, regardless of composite.

Discussion

Photoinitiator concentration is a fundamental parameter that determines the polymerization characteristics of a composite [7,8]. This concentration is variable among the commercial composite and its effects on polymeric structure of composites is not still completely elucidated [23].

In this study the variation on concentration of photoinitiators affected all the evaluated properties, confirming the tested hypothesis. The composites with higher concentration of CQ/DMAEMA (C2 and C3) showed higher DC than the composite with lower concentration (C1). In addition, the depth of cure was also higher for C2 and C3 than for C1. What means that, the presence of a higher quantity of photoinitiators

Table 3 Results of indirect evaluation of cross-link density, expressed in percentage of softening after storage in ethanol (%) in relation to type of composite and photoactivation method, means (SD)

	C1	C2	C3
HI	41,2 (14,98) ABa	34,6 (07,61) Bab	26,1 (11,59) Bb
LI	37,0 (08,39) Bb	49,8 (08,50) Aa	41,0 (11,53) Aab
SS	50,7 (09,73) Aa	46,4 (09,33) ABa	42,8 (08,30) Aa
PD	35,6 (09,28) Ba	44,6 (11,26) ABa	42,8 (10,76) Aa

Statistical differences are expressed by different capital letters in columns, and by different minuscule letters in rows ($p < 0.05$).

Table 4 Results of depth of cure (DCure) in relation to type of composite (C) and photoactivation method (PM), means (SD)

PM	C	Surface	1 mm	2 mm	3 mm	4 mm	DCur
HI	C1	35.8(1.67)Ca	37.1(3.13)Ca	21.5(3.61)Cb	02.8(0.62)Cc	00.0(0.00)Cd	1 mm
	C2	51.5(2.49)Ba	46.2(1.09)Ba	44.9(2.59)Ba	25.3(3.54)Bb	02.9(0.22)Bc	2 mm
	C3	56.8(3.31)Aa	58.4(2.37)Aa	52.9(1.54)Aa	48.2(1.88)Aa	20.4(2.50)Ab	3 mm
LI	C1	35.0(1.66)Ca	34.0(2.56)Ca	16.0(4.50)Cb	02.8(1.54)Cc	00.0(0.00)Ac	1 mm
	C2	43.4(0.67)Ba	43.2(5.43)Ba	36.2(2.61)Ba	17.4(5.97)Bb	02.2(0.43)Ac	2 mm
	C3	56.1(9.11)Aa	53.9(4.89)Aa	49.3(6.07)Aa	29.5(6.59)Ab	06.8(3.97)Ac	2 mm
SS	C1	34.1(3.67)Ca	32.5(2.83)Ca	13.3(3.74)Cb	02.9(0.69)Cc	00.0(0.00)Bc	1 mm
	C2	41.5(2.07)Ba	40.3 (2.95)Ba	38.8(5.23)Ba	28.3(5.48)Bb	06.8(2.51)ABc	2 mm
	C3	48.0(3.34)Aa	47.4(2.34)Aa	46.2(5.61)Aa	40.8(3.18)Aa	12.7(3.46)Ab	3 mm
PD	C1	33.0(2.96)Ba	33.5(2.87)Ba	17.8(1.88)Bb	03.6(1.51)Cc	00.0(0.00)Bc	1 mm
	C2	47.4(6.25)Aa	47.0(8.90)Aa	42.6(4.61)Aa	26.9(4.79)Bb	10.5(8.87)Ac	2 mm
	C3	49.1(5.12)Aa	47.2(1.89)Aa	47.7(2.70)Aa	37.7(5.43)Ab	12.8(4.00)Ac	2 mm

Statistical differences are expressed by different capital letters in columns within each group of PM, and by different minuscule letters in rows ($p < 0.05$).

(CQ/DMAEMA) allows the generation of more radicals, which have resulted increased degree of conversion in some conditions of photocuring. Regarding the parameters analyzed, the most adequate photoinitiator concentration was 1.5 wt% of CQ/DMAEMA. The concentration of 0.5 wt% of CQ/DMAEMA was considered inappropriate for the resin matrix used.

The attempt to find an ideal concentration of photoinitiators for resin materials was the aim of a study from Moin Jan *et al.* [22]. Evaluating degree of conversion and photoinitiators elution, authors claimed that the better concentration of photoinitiators is 0.5% of CQ/DMAEMA in 1:1 proportion. These authors also found a decrease on the DC and increase in composite components elution (especially CQ) in experimental composites with 0.8 e 0.9% de CQ/DMAEMA. At first, this result seems to be divergent to ours, since in this study the composite with 0.5% of photoinitiators showed the worst results. However, the resin monomer system evaluated in Moin Jan *et al.* [22] study was UDMA/TEGDMA (50:50) and no filler particles were included. In the present study, the composite has 65% fillers and a monomer system based on BisGMA/TEGDMA (65:35). As UDMA has lower molecular weight and higher molecular mobility than BisGMA, and the quantity of TEGDMA (diluent monomer) is higher in the Moin Jan material, we could speculate that the Moin Jan material need less concentration of photoinitiators when compared to systems with higher molecular weight, as the system used in the present study. The filler particles also turn the polymerization more difficult, in this way the concentration of photoinitiators should be higher in composites than in resins.

The effect of photoinitiator concentration was also evident in the depth of cure evaluation. The depth of cure for C1 (1 mm, regardless the photoactivation method) was lower than that observed for C2 (2 mm) e C3 (2 mm / 3 mm). In this evaluation, was also verified a significant reduction on KHN with increase of depth for all materials. It is explained by the difficult of light penetration within the composite in the deeper layers, what leads to reduction on conversion degree [24]. Therefore, reduction on degree of conversion in these areas would reduce the KHN. This reduction on KHN was more evident for C1 (0.5% CQ/DAMEMA), which was completely unstiffened (not cured) at

the depth of 4 mm. These results corroborate with Cunha *et al.* [25]. Also, according to Table 3, the hardness of the C3 in all depths was superior or similar to C2, but always higher than C1, what also reveal the superior effectiveness of in composites with higher concentration of photoinitiators.

The results of depth of cure are supported by the results of the DC test, in which the composite with 0.5% of CQ/DMAEMA (C1) presented significant less conversion than the others (C2 and C3). Also, the cross-linking density is increased for composites with higher photoinitiator concentration photoactivated using high irradiance. The combination C3 and HI provided the composite with the best characteristics of polymerization.

Thus, the first tested hypothesis, that the higher concentration of photoinitiator can increase degree of conversion, surface hardness, depth of cure and crosslink density was accepted. The exception occurred when the low concentration composite (C1) was photoactivated with LI, however, it should be considered that C1 showed lower DC when compared to other composites. This difference may explain the different behavior of softening in ethanol between C1 and C2/C3.

Another factor analysed in this study was the photoactivation method. Some studies have shown that photoactivation method can affect the polymerization characteristics of resin composites [10,13,20]. Modulated photoactivation methods can reduce shrinkage stress without interfere with properties such as volumetric shrinkage, degree of conversion, hardness, flexural strength, and others [13,26,27].

In this study photoactivation methods had no influence on degree of conversion, regardless the material, what corroborate whit other studies that employed different photoactivation methods with similar energy dose [13,26,27], validating part of the second tested hypothesis. Low intensity did not reduce degree of conversion because the light exposure time was increased until the polymerization reaches the diffusion limited free radical propagation [27]. It is because the polymerization is controlled by the radiant exposure. Some authors showed degree of conversion is directly related to the radiant exposure (Radiant exposure = Irradiance \times Light exposure) delivered to the material [27,28].

The depth of cure test revealed significant difference among the photoactivation methods for C3 denying the hypothesis that photoactivation methods do not affect the depth of cure. Regarding this material, methods HI and SS showed depth of cure of 3 mm while PD and LI, 2 mm. The likely explanation for this fact is that the long exposure time associated with the reduced irradiance in the first period of the activation increased the conversion at the superior layers and turned difficult the light diffusion within this 2 mm layer, reducing the conversion/KHN at 3 mm. Conversely, for the other photoactivation methods, the initial (for HI) or quick (for SS) exposure of the material to the higher irradiance, allowed easier light incoming into the 2 first mm and similar conversion/KHN on the 3 mm depth.

Differences in network structure determine the ethanol softening, what, after all, is determined by the cross-linking density [13,20,29]. The exposure contact of resin composites with the solvents causes the softening of the polymeric dimethacrylate materials because attraction forces between solvent molecules and polymer chain compounds are stronger than attraction forces among the polymeric chains. The solvent penetrates within the resin matrix and expand the openings among the chains, allowing elution of residual monomers and dissolution of the linear chain [29,30]. The penetration ability

of the solvent is related to its solubility parameter (ability of a molecule in penetrating and dissolving another substance). The difference in solubility parameters between polymers and solvents determines the softening of the polymer matrix: the lower the difference the higher the solvent penetration into the polymer network, the higher the softening [29,30]. For composites, solubility parameter is related to formulation (monomers type/concentration) and networking (cross-linking density). More linear polymeric chains would be more degraded by the ethanol than more crosslink chains [30]. It is because, solvent may form strong secondary bond with polymer chains, replacing secondary bonds among chains (dissolution of linear polymeric network). Such polymer-solvent secondary bond, however, cannot overcome primary valence cross-link, consequently the cross-linked polymers are less soluble, reducing the softening of the network. Additionally, cross-links prevent solvent molecules from establishing adequate interactions with the polymer thus preventing the molecules to be carried off into solution [30]. In this study, all groups showed, in more or less extension, significant degradation/swelling/softening after 24 h ethanol storage.

The photoactivation using high intensity seems to provide a polymeric matrix more resistant. The softening in ethanol of the specimen photoactivated using HI was significantly inferior to those observed in the specimen photoactivated using LI, for all materials. For C3, HI also showed significant reduction on softening when compared with SS and PD. As the radiant exposure has been the same (28 J/cm^2) for all methods, this result suggests difference in cross-linking density among the methods. Possibly, the activation using continuous light in high intensity started multiple chain propagation centres, what generates higher degree of cross-linking [30]. Highly cross-linked polymers tend to be harder, inflexible, more heat-resistant and more fracture-resistant [31]. This result validates the second part of the second hypothesis.

Composites polymerized using low irradiance or using modulated photoactivation methods showed polymeric network less resistant to ethanol softening, which corroborate with previous studies, in which activation using low intensity (just initially or during the total light exposure) were associated to the fewer chain propagation centres, allowing the formation a more linear network [13,20,30]. Probably, this network presents less cross linking and more primary cyclization. The primary cyclization reactions create micro-gels and lead to heterogeneity in the polymer network where loosely cross-linked regions and more highly cross-linked micro-gel regions coexist. This cyclization will promote higher local conversion as it does not decrease the mobility of the system as much as cross-linking. However, cyclization can also lead to a reduction in the effective cross-linking density, since cycles do not substantially contribute to the overall network structure. According to Brandt *et al.* [13], irradiance, more than radiance exposure, determines the behaviour of the composite after ethanol storage.

Another aspect to discuss is depth of cure reached by specimen photoactivated using low irradiance. Cunha *et al.* [25] stated that the hardness not only depends on the amount of energy but also on the irradiance. Considering that, if the irradiance is reduced at the surface, it could be expected a more intense reduction on this intensity when the light passes through the composite. So, it could be expected that the method that uses low intensity (LI) would present a more accentuated reduction on KHN at the deeper areas than the other methods. However, it not occurred. As the exposure radiant was adjusted the all photoactivation methods, the polymerization depth obtained

for all methods was quite similar. Therefore, it could be hypothesized that the regulating factor for depth of cure is the radiant exposure, and if this dose were adjusted even using a low intensity, as 150 mW/cm^2 , the polymerization will have a pattern similar or even better than that observed for other PM.

According to the results of this study, composites with different concentration of photoinitiators show different polymerization behaviour. And, despite of the benefits of stress reduction obtained with modulated photoactivation methods or low-intensity method, it should be considered that there is a possibility of decrease on mechanical properties and low resistance to chemical degradation of the polymer matrix due to the formation of a more linear structure (low cross-linking). Thus, only the understanding of the causes of problems associated to development of techniques to reduce their consequences would help the clinicians to obtain the maximum benefits of composite restorations in clinical practice.

Conclusion

- 1) Photoinitiator concentration was the determinant factor on polymerization characteristics of the composites. Higher concentration of photoinitiators (C2 and C3) increased the conversion degree and the depth of cure.
- 2) Photoactivation methods had no effect on the degree of conversion, as the same radiant exposure was used for all methods.
- 3) Composites cured using modulated photoactivation methods (SS e PD) or continuous light in low intensity (LI) showed lower crosslink density when compared to composites cured using continuous light in high intensity (HI) for composite with higher concentration of photoinitiators.

Competing interests

The authors declare that they have no competing interests.

Author's contributions

RCBA carried out the depth of cure, the crosslink density, participated in the sequence alignment and drafted the manuscript. WCB carried out the manipulation of composites, analyzes the degree of conversion, participated in the sequence alignment and drafted the manuscript. EJCS-J participated in the sequence alignment and drafted the manuscript. RMP-R participated in the sequence alignment and drafted the manuscript. MACS participated in the sequence alignment and drafted the manuscript. All authors read and approved the final manuscript.

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