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Original Article

Influence of Different Photoinitiators on Polymerization Kinetics and Marginal Microleakage in Restorations using Photopolymerizable Dental Composites

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Abstract

Objective: To evaluate the influence of four different photoinitiators on the polymerization kinetics and marginal microleakage in class V restorations using photopolymerizable dental composites. **Material and Methods:** Four photopolymerizable dental composites based on Bis-GMA (14.5 wt %), UDMA (6.5 wt %) and silanized filler particles (79 wt %) containing different photoinitiators were formulated. Camphorquinone (CQ)/amine, phenyl-propanedione (PPD), monoacylphosphine oxide (Lucirin® TPO) and bisacylphosphine oxide (Irgacure® 819) were used as photoinitiators. Sixteen intact human third molars were selected and divided into four groups. All teeth received class V cavity preparations in their buccal and lingual surfaces and were submitted to a dye leakage test. Data were independently analyzed for both enamel and dentin, and the results were assessed by a Kruskal-Wallis test. The polymerization reactions of the four composites were evaluated by differential scanning calorimeter coupled with photocalorimeter accessory. **Results:** Lucirin® TPO presented the highest scores for microleakage in enamel, whereas the other photoinitiators have not demonstrated statistical differences. The lowest scores were obtained for PPD in dentin while the highest scores have been achieved by Irgacure® 819 and Lucirin® TPO. Photocalorimetric measurements demonstrated a correlation between polymerization reaction rate and marginal leakage, showing that faster reactions cause greater marginal leakage. **Conclusion:** Marginal microleakage scores in photopolymerizable dental composites can be greatly influenced by different types of photoinitiators through their distinct reaction rates.

Keywords: Photoinitiators, Dental; Composite Resins; Dental Leakage.

Introduction

Photopolymerizable composites in dental restorations have been increasingly used worldwide in the last decades due to their excellent aesthetics, biocompatibility, good mechanical properties and easy handling [1]. These materials are essentially composed of two phases: an organic resinous matrix, comprising dimethacrylate monomers, photoinitiator and other minor additives and an inorganic phase, known as filler, generally composed of Barium aluminum silicate particulate glass and pyrogenic silica normally surface modified by a coupling agent aiming to improve the mechanical properties after polymerization [2].

The most common monomers found in the resinous phase are bisphenylglycidyl dimethacrylate (BisGMA), triethylene glycol dimethacrylate (TEGDMA) and urethane dimethacrylate (UDMA). The photoinitiator system is typically camphorquinone associated with a tertiary amine [2].

Although photopolymerizable dental composites present numerous advantages in dentistry compared to other restorative materials, several issues are still reported including low color stability, low abrasion resistance and shrinkage during polymerization, which may create marginal gaps leading to microleakage and consequently secondary cavities [3-9]. As shrinkage is directly related to the way a composite polymerizes [6], the study of different photoinitiators can help reduce or even eliminate the occurrence of marginal gaps and consequently microleakage [10,11], improving the quality and stability of the final restoration.

Thus, the aim of the current study was to establish a correlation between polymerization reaction rate using photopolymerizable composites with four different photoinitiators and marginal microleakage in class V restorations prepared with these composites.

Material and Methods

This study was approved by the Ethics Research Committee of the FUNORTE University under protocol number 003/08.

Four photopolymerizable dental composites formulate with different photoinitiators were supplied by Biodinâmica – Brazil with the following base composition according to the manufacturer: Monomers: (1-methylethylidene)bis[4,1-phenyleneoxy(2-hydroxy-3,1-propanediyl)] bismethacrylate (BisGMA) - 14.5 wt% and Isopropylidenediphenyl Bisoxhydroxypropyl Methacrylate, mixture of isomers (UDMA) - 6.5 wt%. Filler: Inorganic silanized particles composed of a mixture of ground glass and pyrogenic silica with size ranging from 0.04 to 2.20 μm (79 wt%). The brands of monomers and fillers were omitted by Biodinâmica considering they are part of issues related to industrial secrets. Four different photoinitiators were added separately to this base formulation at molar concentration of 6.0×10^{-3} mol/g (mols of photoinitiator per gram of monomers). DL-bornane-2,3-dione (Camphorquinone or CQ, Sigma-Aldrich®); 1,2-phenylpropanedione (PPD, Sigma-Aldrich®); 2,4,6-Trimethylbenzoyldiphenylphosphine oxide (Lucirin® TPO, BASF); and Phenyl bis(2,4,6-trimethylbenzoyl)-phosphine oxide (Irgacure® 819, BASF), as shown on Table 1. Additionally,

benzoic acid, 4-(dimethylamino)-, ethyl ester (DMABEE) was added at concentration of 9.0×10^{-3} mol/g as co-initiator to composite containing CQ since it is a type-II photoinitiator.

Table 1. Photoinitiators and their molecular mass, λ_{\max} of maximum absorption and concentrations.

Photoinitiator	Molecular Mass	λ_{\max} (nm) of maximum absorption	Concentration mol/g	Concentration wt%
Camphorquinone	166	470	6.0×10^{-3}	0.100
DMABEE	193		9.0×10^{-3}	0.175
PPD	148	398	6.0×10^{-3}	0.088
Lucirin TPO	348	381	6.0×10^{-3}	0.208
Irgacure® 819	418	370	6.0×10^{-3}	0.250

Sixteen human molar teeth were selected and randomly divided into 4 groups of 4 teeth each. Class V cavities were prepared on the buccal and lingual surfaces of each tooth, with occlusal margins in enamel and cervical margin in dentin, located 1.5 mm below the cement-enamel junction. Preparations were standardized and had the following dimensions: 4.0 mm in width, 3.0 mm in height and 1.5 mm in depth. Diamond burs used were discarded every 4 preparations.

Cavities were etched with 37% phosphoric acid (3M Co., St. Paul, MN, USA) for 15 seconds in dentin and 30 seconds in enamel, followed by water rinsing for 1 minute, subsequently dried with absorbent paper. The Single Bond adhesive system (3M Co., St. Paul, MN, USA) was applied according to manufacturer instructions and then polymerized for 40 seconds using QTH (quartz tungsten halogen) light curing unit (Optilight 600, Gnatus, Ribeirão Preto, SP, Brazil) with irradiance of 600 mW/cm².

Cavities were filled with composites formulated in this study according to the incremental technique. The first increment was applied onto the gingival wall; the second onto the occlusal wall, and the third was placed to restore the tooth outline. Each increment was light cured for 40 seconds. After polymerization of the third increment, an oxygen insulator was applied on the restoration and it was light cured for an additional time of 40 seconds. Restorations were then polished with Sof-lex discs (3M Co., St. Paul, MN, USA) as a finishing procedure. At the end, 8 restorations were made for each group and tested in different teeth (n=8). All specimens were then stored in a 100% humidity environment, with temperature of 37°C for 14 days. Finally, they were submitted to 1,500 thermocycles with temperatures ranging from 5 to 55°C, in an immersion period of 30 seconds and translation periods of 10 seconds.

Microleakage was assessed using the dye penetration technique. Teeth had their apices and restoration area sealed with an epoxy resin layer, followed by the application of two layers of nail varnish, ranging 1.0 mm from the cavosurface angle. Twelve hours after sealing, specimens were immersed in 2% Methylene Blue solution with pH = 7.2 for 24 hours at 37°C.

Teeth were longitudinally sectioned in a buccal-lingual direction through the center of the restorations and their surface was smoothed with sandpapers of 200, 400 and 600 granulations. Eight specimens were used for each group (n=8).

Microleakage was determined by dye penetration from the cavosurface angle to the axial wall, through gingival and occlusal walls using criteria shown in Table 2. Subsequently, all specimens were examined with 10x binocular stereoscopic magnifying glass by three examiners who did not know which filling material had been used in each tooth. Occlusal and gingival walls were assessed separately. The teeth halves were examined separately and the highest microleakage score was considered. Results obtained were submitted to Kruskal-Wallis (K-W) test, considering alpha as 0.05.

Table 2. Criteria to determine dye penetration scores.

Score	Definition
0	No dye penetration
1	Dye penetration up to 1/3 of the horizontal cavity wall
2	Dye penetration up to 2/3 of the horizontal cavity wall
3	Dye penetration beyond 2/3 of both horizontal and axial walls

Polymerization rate was evaluated in real time using a Differential Scanning Calorimeter – Model DSC Q100 (TA Instruments®) coupled to a Photocalorimeter Accessory – PCA (TA Instruments®) equipped with high-pressure mercury lamp. The wavelength was adjusted between 390 and 500 nm using cut-off filters to simulate the QTH Lamp spectrum. The maximum irradiance achieved was 250 mW cm², the irradiation time was 180 seconds and the purge gas was nitrogen (flow of 75 ml min⁻¹). For each resin, 15.0 mg were weighed in an open aluminum pan and the DSC-PCA cell was thermostated at 25°C. Data were acquired by TA Universal Analysis Software. By integrating the curves, the total heat released vs. time for each sample was obtained, which is an indirect measurement of the degree of conversion (DC). Fitting a straight line to the ascending part of curves, acceleration of the polymerization reaction was obtained, which indicates how fast it occurs. Five measurements were conducted for each group tested (n=5), and the results were statistically assessed using the ANOVA test (p=0.05).

Results

The K-W test was applied to enamel and dentin independently using the photoinitiator as variable, and the marginal microleakage as variation factor.

By considering the enamel on the K-W test, a difference between groups can be verified (p=5%) as shown on Table 3. Paired comparison between groups showed no difference among CQ, PPD and Irgacure® 819. Lucirin® TPO showed a significantly higher microleakage score in enamel when compared to other groups.

Table 3. Microleakage scores in enamel and Kruskal-Wallis test results.

Photoinitiator	Scores				Statistical Analysis
	0	1	2	3	
CQ	8	-	-	-	A
PPD	8	-	-	-	A
Lucirin® TPO	5	2	1	-	B
Irgacure® 819	8	-	-	-	A

Same letter is not statistically different (p>0.05).

Considering dentin on the K-W's test, a difference was verified between groups ($p= 5\%$) as shown in Table 4. PPD showed significantly lower marginal microleakage scores when compared to the other groups.

Table 4 shows that the highest microleakage scores occurred in CQ, Lucirin® TPO and Irgacure® 819. No significant differences were found between CQ and Lucirin® TPO or between Lucirin® TPO and Irgacure® 819. It was also observed that microleakage was significantly lower in CQ than in Irgacure® 819.

Table 4. Microleakage scores in dentin and Kruskal-Wallis test.

Photoinitiator	Scores				Statistical Analysis
	0	1	2	3	
CQ	3	-	-	5	A
PPD	5	-	1	2	B
Lucirin TPO	1	-	-	7	A,C
Irgacure® 819	-	-	-	8	C

Same letter is not statistically different, $P>0.05$).

Regarding photocalorimetry in Table 5 and Figure 1, Irgacure® 819 obtained the highest results on both released heat and reaction speed, followed by Lucirin® TPO. CQ obtained the lowest results for released heat, and PPD demonstrated a significantly slower reaction speed than the other photoinitiators tested.

Table 5. Values obtained through photocalorimetric measurements.

Photoinitiator	Peak Time (s)	Released Heat ($J g^{-1}$)	Reaction Acceleration ($J g^{-1} s^{-2}$)
CQ	2.3	27.16 ± 1.0^a	3.26 ± 0.5^a
PPD	17	27.92 ± 1.0^a	0.58 ± 0.2^b
Lucirin TPO	1.2	30.31 ± 0.3^b	10.74 ± 0.7^c
Irgacure® 819	0.9	44.93 ± 1.7^c	15.25 ± 1.1^d

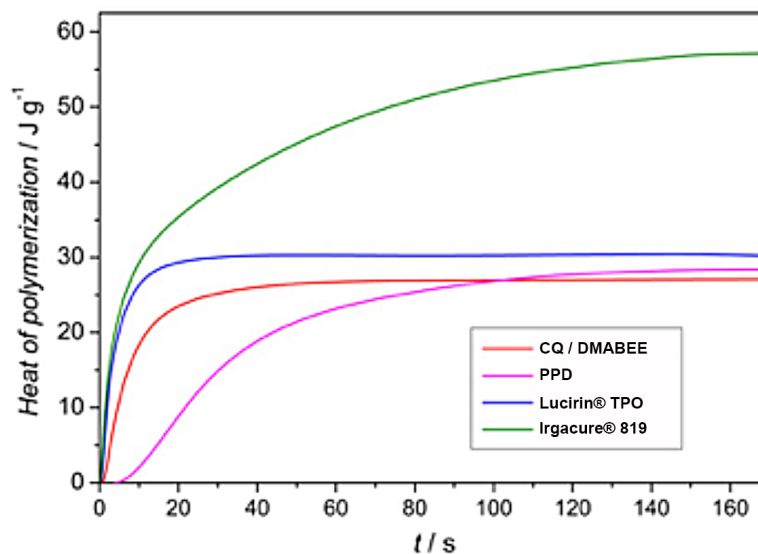


Figure 1. Heat of polymerization vs. time.

Discussion

Polymerization shrinkage is an undesirable effect that occurs in resin-based restorative materials. Their shrinkage may cause adhesive interface de-bonding, post-operative pain, marginal discoloration, recurrent caries and restorations losses [13,14]. Dye penetration test is recommended to anticipate material's clinical performance, being therefore the main technique used to evaluate marginal microleakage [13].

A slow-cure composite resin is preferable, since it can reduce shrinkage stress, preserving marginal integrity [16]. Nevertheless, shrinkage and conversion are closely related manifestations of the same process. Resin showing high conversion score will also show high shrinkage. Thus, attempts have been made to decrease the process speed during the initial moments of reaction, so that polymerization stress can be dissipated [16]. In the present study, Lucirin® TPO and Irgacure® 819 obtained the highest released heat values and, consequently, the highest DC values. These photoinitiators were also those that obtained the highest marginal microleakage values.

Slower polymerization can be achieved by using the soft start curing technique, where lower light intensity is used at the beginning of the polymerization period [7,16]. Another method is called pulse delay curing, where polymerization is initiated by a short flash of light, followed by a stand-by period before final photoactivation [17]. In both cases, gap formation reduction was observed, without compromising mechanical properties. Paradoxically, considering a composite resin, a relatively slow polymerization with high level of final conversion is desired.

The stress generated depends on the polymerization reaction kinetics [14], which may be affected by a number of factors such as: type and intensity of light source, load type [18], shades [16], initiator's concentration (diketone), co-initiator (tertiary amine) and presence of inhibitor, or even by the type of monomer used [19].

The most popular photoinitiator among dental polymers is camphorquinone (CQ) [2,10,20-27]. CQ has good absorption within the visible region of the light spectrum, with wavelength peak of 470 nm [10]. Since it is a Type-II photoinitiator, camphorquinone has better performance as photosensitizer, requiring the presence of co-initiator to increase the efficiency in the production of free radicals. As a result, tertiary amines are added to it, acting as reducers or hydrogen donor agents.

CQ concentration of 0.1 wt% was chosen for the present study because it is in accordance with findings of previous studies [2,25]. However, the other photoinitiators tested showed different molecular masses (Table 1). Concentration according to molar mass was adopted (mol.g-1) to standardize the photoinitiator concentration according to the number of molecules available for reaction. Considering that 0.1%w/w of CQ equals 6×10^{-6} mol g-1, this molar concentration was adopted for the other photoinitiators (Table 1).

CQ has been successfully used as a photosensitizing agent for composite resins. Unfortunately, it has some undesirable properties, such as the yellowing effect due to incorporation and also its need for a tertiary amine, which may cause future material discoloration [2]. These

factors have stimulated researches to find new photoinitiator agents with better properties like PPD, Lucirin® TPO and Irgacure® 819. These are Type-I photoinitiators, which generate free radicals through the cleavage of their molecules, without requiring a co-initiator. In addition, they cause less yellowing than CQ. In the present study, CQ obtained intermediate results regarding polymerization kinetics, demonstrating a faster reaction than that showed by PPD, although it showed slower scores than those presented by Lucirin® TPO and Irgacure® 819. On the other hand, its microleakage results also showed intermediate values.

PPD is a Type-I photoinitiator, so it generates free radicals via photocleavage in a more efficient way, eliminating the need for co-initiator [20]. Several studies [12,19,20,23] have demonstrated that PPD works as an effective photoinitiator (comparable to CQ) in order to initiate the polymerization reaction for dental resins.

Some authors [19] observed that the polymerization of resins with PPD, when compared to camphorquinone, occurs in a slower way. These authors observed that the polymerization shrinkage observed during periods of 3 and 10 seconds was smaller in PPD, but the final shrinkage rate at 120 seconds of irradiation was similar. Previous studies [27,28] have found a strong correlation between shrinkage stress and marginal microleakage in class V cavities. In the present study, PPD showed the lowest microleakage indexes in dentin, and similar to CQ and to Irgacure® 819 in enamel. As its polymerization shrinkage is slower, PPD has compensated better the shrinkage stress of the composite resin during the initial moments of reaction, similarly to what occurs in gradual photoactivation techniques, such as soft star and pulse delay [19,29].

Other photoinitiators studied derive from bis-aquid phosphinic oxide (BAPO, or Irgacure® 819) and mono-aquid-phosphinic oxide (MAPO or Lucirin® TPO). These Type I photoinitiators show light absorption peak in the UV band; however, they show good absorption in the visible band [12]. Acylphosphine oxides undergo fast photolysis of the carbon-phosphorus bond, generating benzoyl and phosphonyl radicals, both very reactive and able to initiate polymerization [10,30]. As they are more efficient, acylphosphine oxides promote polymerization process faster than CQ, leading to higher conversion values. For this reason, the stress generated by its shrinkage is higher, which may lead to greater lack of marginal adaptation.

In the present study, both Lucirin® TPO and Irgacure® 819 have shown the worst scores for dentin microleakage, demonstrating greater gap formation during polymerization. In enamel, the worst results have also been shown by Lucirin® TPO, whereas Irgacure® 819 was similar to CQ and to PPD. Irgacure® 819 presents higher potential to form free radicals, up to four reactive radicals, compared to the two presented by the Lucirin® TPO molecule and the only one by CQ [10,11]. On the other hand, some authors [11] demonstrated that Lucirin® TPO shows quantum yield polymerization four times higher when irradiated by QTH LCU. Therefore, the Lucirin® TPO reaction occurs faster when halogen lamp is used, justifying the higher microleakage indexes in enamel found in the present study. As it is not possible to couple QTH LCU to the calorimeter, a photocalorimetry accessory was used in this study. In this apparatus, a filter was added to obtain

light spectrum as close as possible to that found in QTH LCU. Although irradiation of 250 mW/cm² was lower than that in QTH LCU, it agrees with this technique. The light heat was compensated by previous DSC calibration.

The polymerization patterns of resins containing the new photoinitiators depend on the light sources used. The narrow emission spectrum of LEDs LCUs suggests that these units are not quite appropriate for these photoinitiators. Contrarily, QTH LCU shows a better overlap with the absorbance of PPD, Lucirin® TPO and Irgacure® 819. This indicates that the light source should be chosen according to the photoinitiator used [7,10,30].

The polymerization kinetics results showed a direct correlation with the dye infiltration test. In a faster polymerization reaction, as obtained by Lucirin® TPO and Irgacure® 819, the shrinkage stress is higher, leading to poor marginal adaptation and consequently microleakage. On the other hand, PPD showed slower polymerization reaction, which allows greater tension release, resulting in better resin adaptation to the cavity wall and consequently lower microleakage index. CQ obtained intermediate scores for even polymerization kinetics and dye infiltration.

Conclusion

Within the limitations of the present study, it was possible to prove that photoinitiators with different reaction kinetics can alter marginal microleakage scores in composite resin. However, further investigation is required in order to evaluate mechanical performance and the clinical longevity of these photoinitiators in resin-based dental materials.

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