

Effect of the photoinitiator system on the properties of a dental material based on a hybrid polymer

Efeito do sistema fotoiniciador sobre as propriedades de um material dentário baseado em um polímero híbrido

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ABSTRACT

Objective: In this study, the effects of two different cure protocols upon the properties of composites using a hybrid-polymer as dental resin were evaluated. **Material and Methods:** Two distinct dental composites were prepared, one containing a mixture of TEGDMA/bis-GMA (50:50) and, another containing a mixture of TEGDMA/p-MEMO (50:50), [p-MEMO: oligomeric inorganic precursor]. Both composites were polymerized with lucirin and canthorquinone as photoinitiators. The composites were made with a 70 % wt of inorganic filler. Flexural strength was evaluated with a universal test machine and the degree of conversion was measured by infrared spectroscopy. A helium pycnometer was used to obtain polymer shrinkage data. Sorption tests were performed and SEM microscopy was used to show deleterious effects upon the resins' surfaces. **Results:** The sample based on TEGDMA/p-MEMO polymerized with lucirin (L-T/p) showed the best values of the monitored properties. **Conclusion:** Lucirin is the most suitable photoinitiator for dental composites containing hybrid polymers.

KEYWORDS

Dental resins; Flexural strength; Hybrid polymer; Photoinitiator system; Polymerization shrinkage.

RESUMO

Objetivo: Nesse estudo, foram avaliados os efeitos de dois diferentes protocolos de cura sobre as propriedades de um compósito usando um polímero híbrido como resina dentária. **Material e Métodos:** Dois compósitos diferentes foram preparados, um contendo uma mistura de TEGDMA/Bis-GMA (50:50) e, outro contendo uma mistura de TEGDMA/p-MEMO (50:50), [p-MEMO: precursor oligomérico inorgânico]. Ambos compósitos foram reticulados com lucirin e canforoquinona. Os compósitos foram preparados com 70% em massa de carga inorgânica. Resistência flexural foi avaliada com uma máquina de testes universal e o grau de conversão calculado por espectroscopia na região do infravermelho. Um picnômetro a gás hélio foi usado para obter os dados de contração de polimerização. Testes de sorção foram feitos e microscopia eletrônica de varredura foi usada para avaliar efeitos deletérios sobre as superfícies das resinas. **Resultados:** A amostra constituída com TEGDMA/p-MEMO reticulada com lucirin (L-T/p) apresentou os melhores valores das propriedades monitoradas. **Conclusão:** Lucirin é o sistema fotoiniciador mais adequado para compostos dentários contendo polímeros híbridos.

PALAVRAS-CHAVE

Resinas dentárias; Resistência flexural; Polímero híbrido; Sistema fotoiniciador; Contração de polimerização.

INTRODUCTION

A restorative dental composite is mainly constituted of three different parts: a) an organic matrix to give flexibility and good handling for the cavity to be completely filled and to connect the dispersed phase (silica); b) inorganic inclusions, which represents 65-85 % of the composite, to improve the mechanical properties and give dimensional stability; c) a photoinitiator system that produces free radicals that will initiate the polymerization process of the monomer by using a radiation source, leading to the formation of the three-dimensional networks [1].

In 1962, Bowen [2] developed a monomer to be used in dental composites: the 2,2-bis[4-(2-hydroxy-3-methacryloxyprop-1-oxy)phenyl]propane (bis-GMA). Figure 1a shows its chemical structure.

The stiffness of the composite is due to the presence of aromatic rings. A faster curing process and less intense polymerization shrinkage are the result of its high molecular weight and bifunctionality. The higher the molecular weight, the lower the volumetric shrinkage, as those monomers, with relatively high molecular weight, have low numbers of polymerizable groups per volume unit [3]. Furthermore, these properties also provide a three-dimensional network with greater hardness than the acrylate materials previously used [2].

The high viscosity of bis-GMA (800 to 1200 Pa.s) limits the addition of filler particles. To overcome this drawback, the combination of diluent monomers to reduce the viscosity of the matrix is frequently used. This allows for the addition of higher amounts of inclusion leading to enhanced mechanical properties. Figure 1b also shows the chemical structure of the diluent monomer triethyleneglycol dimethacrylate (TEGDMA).

TEGDMA has a low viscosity and forms mixtures with bis-GMA in various mass proportions in order to obtain heavily loaded

composites that have increased hardness and mechanical strength. The diluent property of TEGDMA may be related to flexibility of its chains which have ether linkages that allow free rotation of methacrylate groups [3]. However, the addition of diluent monomers also causes an undesirable effect: the increase of polymerization shrinkage [4,5].

Research on related organic-inorganic hybrid polymers, also called Organically Modified Ceramics – Ormocer®, suggests the application of these materials as an alternative to the composite conventionally used in dental restoration [6-8].

The properties of hybrid polymers are complementary, combining the mechanical stability and chemical inertness of ceramics with the flexibility inherent to the organic polymers [9,10]. The compound (3-methacryloyloxypropyl)trimethoxysilane (MEMO) can be used as a monomer precursor to produce dental resins due to its methacrylate groups, also shown in Figure 1c.

Organically modified ceramics can be found in commercial resins used for dental restoration such as Admira® (Voco, Germany), a product that has been available on the market for over a decade and, which possesses good mechanical properties such as flexural strength as well as adequate adhesion to teeth [11,12].

This study evaluated the possibility of using an inorganic oligomeric precursor, the polycondensed (3-methacryloyloxypropyl)trimethoxysilane, hereafter called p-MEMO as dental resin. To achieve this goal, p-MEMO was mixed with a diluent monomer and tested using two different photoinitiator systems, i.e., camphorquinone and lucirin. The properties evaluated were flexural strength (FS in MPa), degree of conversion (DC in %), and polymerization shrinkage (PS in %). Aspects related to leaching of the composites were monitored via water sorption (W_{sp} in $\mu\text{g}.\text{mm}^{-3}$) and water solubility (W_{sl} in $\mu\text{g}.\text{mm}^{-3}$) tests and by micrographs of the surface of the cured samples.

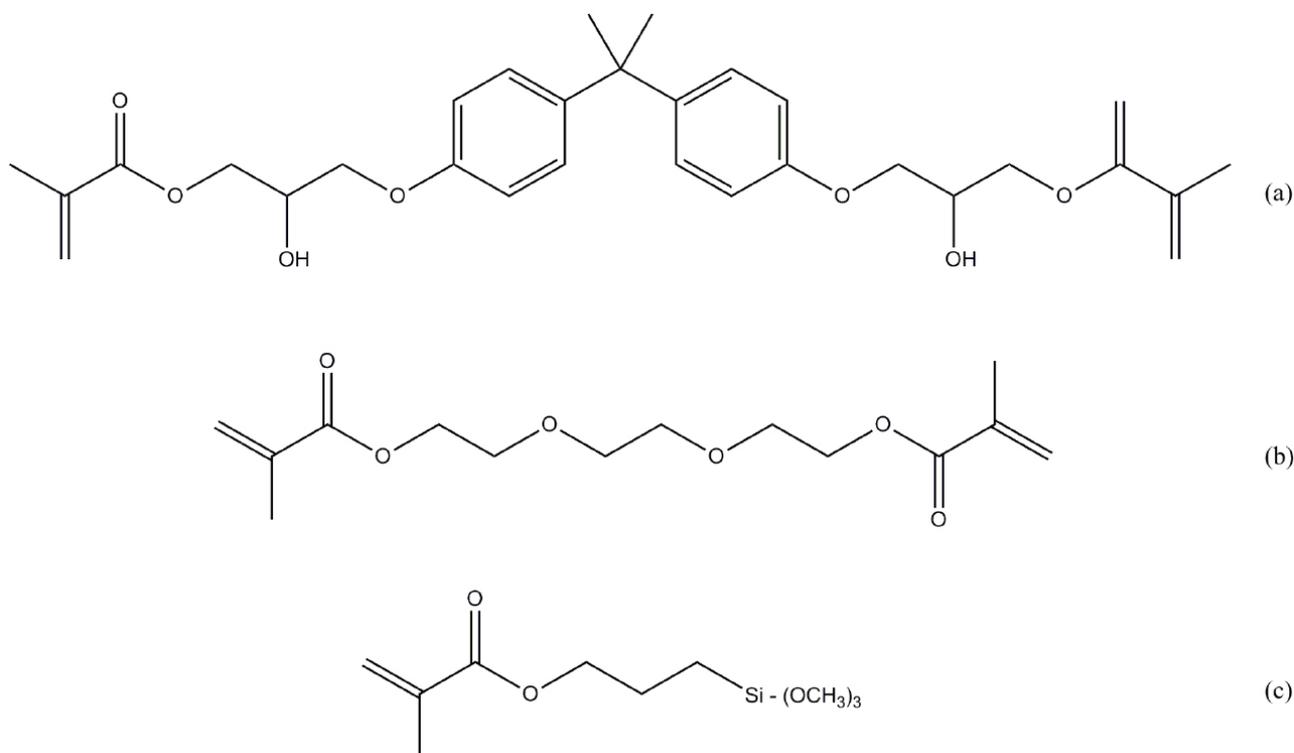


Figure 1 - Chemical structure of (A) bis-GMA, (B) TEGDMA, (C) MEMO.

MATERIAL & METHODS

Bis-GMA (100 %), MEMO (98 %), TEGDMA (95 %), and all other reagents used in this study were purchased from Sigma-Aldrich. The oligomeric inorganic precursor (p-MEMO) was obtained from MEMO by a sol-gel process [13]. Camphorquinone (CQ, 97 %) with 2-(dimethylamino) ethyl methacrylate (DMAEMA, 99 %), and 2,4,6(trimethylbenzoyl) diphenyl phosphine (lucirin, 97 %) were used as photoinitiator systems. Silica was used as the inorganic inclusion (V117 1075, E-3000, 7,5 μm) and was kindly provided by Esstech Inc. All materials were used as received.

Preparation of composites

Specific amounts of the monomers were weighed in petri dishes, and the photoinitiator system was subsequently added, as shown in Table 1.

For curing the composites, 0.8 % w/w of camphorquinone and 3.2 % w/w of DMAEMA

related to the mass of the monomers were used. Lucirin (Norrish type 1 photoinitiator system), in an amount of 1.68% in relation to the weight of the organic matrix, was used as well. These amounts of photoinitiators were calculated so that there was the same molar amount in all formulations. After that, silica (70% of the mass of the composite) was weighed and added in small portions to the Petri dish, and the mixture was homogenized manually with a stainless steel spatula.

Characterization techniques

FTIR: Degree of monomer conversion

To assess the degree of conversion, the samples were irradiated for 180 s (3 pulses of 60 s) on each side with a light-emitting diode

Table 1 - Resin composition in mass percentage

C-T/p	50% TEGDMA + 50% p-MEMO	Camphorquinone
C-T/B	50% TEGDMA + 50% bis-GMA	Camphorquinone
L-T/p	50% TEGDMA + 50% p-MEMO	Lucirin
L-T/B	50% TEGDMA + 50% bis-GMA	Lucirin

(LED) photopolymerization unit (440-480 nm, 1200 mW.cm⁻²) inserted into a mold that was 2.0 mm thick and 7.0 mm in diameter for samples containing camphorquinone. Only the degree of conversion of samples C-T/p and C-B/p was already measured, as described by Venter et al [13]. For the samples containing lucirin, the same cure protocol was used, but the curing unit was a halogen bulb (400-500 nm, 420 mW.cm⁻²). This irradiation protocol was chosen to ensure a maximum degree of conversion of the samples. The irradiated samples were left in a desiccator for 24 h and were pulverized to produce KBr pellets. The spectra in the infrared region of the non-photopolymerized resins were generated on NaCl windows. A Bomem spectrophotometer MB-100 Hartmann & Braun was used. To calculate the degree of conversion, the reduction in peak intensity related to the stretching of the aliphatic C = C bond was compared to the internal referential band of C = O bond stretching. The degree of conversion (DC) was obtained according to Equation 1, where R = intensity of the band at 1640 cm⁻¹ / intensity of the band at 1720 cm⁻¹ [14].

$$DC (\%) = 100 \times \left[1 - \left(\frac{R_{polymer}}{R_{monomer}} \right) \right]_{(1)}$$

Flexural strength

The flexural strength of the dental materials was evaluated according to ISO 4049, using specimens in the form of rods with dimensions of 25 mm x 2 mm x 2 mm. After preparation, a specimen was immersed in water at 37 °C for 24 h. For the trials, the samples were dried with soft paper and led to a testing machine (Lloyd Instruments LR 10K plus).

Polymerization shrinkage

Polymerization shrinkage was measured by the difference in volume of the composites before and after irradiation. For this analysis, a helium gas pycnometer (Multipycnometer, Quantachrome Instruments) was used. Initially, disposable aluminum cups were prepared and their volume was measured. Uncured samples

were then added to these containers and the volume was measured again. The volume of a non-polymerized sample (V_m) was obtained by deducting the value of the aluminum cup's volume. The cup with the uncured sample was then removed from the measuring chamber, and the curing procedure was performed with 6 pulses of 60 seconds. The cured sample was then left in a lightproof desiccator for 24 h. Soon after, the measurement of the cured sample was performed by again deducting the volume of the aluminum cup, the cured sample volume (V_p) was obtained. The dimensional change or polymerization shrinkage (PS) was then determined by the relation between the average values of the polymerized (V_p) and monomeric materials (V_m). Thus, the change undergone by a material during curing was determined by applying Equation 2.

$$PS (\%) = 100 \times \left[1 - \left(\frac{V_p}{V_m} \right) \right]_{(2)}$$

Water sorption and solubility tests

The preparation of composites for sorption and solubility testing in water followed the ISO standard 4049. Portions of the uncured composite were added in a single increment (to avoid the formation of bubbles) to a stainless steel cast, measuring 1 mm in thickness and 15 mm in diameter. A Mylar® strip was placed on top of the mold (surface) to avoid adhesion with the glass plaque (5 mm thick), which was pressed against the mold/composite, in order to obtain a smooth surface. The irradiation was performed according to standard recommendations (ISO 4049), as follow as: each sample had one central pulse and eight overlapping pulses on the surface in both sides of the specimens using the photopolymerization unit early described in FTIR monomer conversion section.

After irradiation, the samples were placed in a lightproof desiccator under controlled temperature (37 °C) and kept until a constant mass (m_1) was achieved. The volume of the discs was calculated by measuring the diameter and thickness with the aid of a digital caliper. Each

disc was placed in a hermetically sealed container with 10 mL of distilled water and then left for 168 h in a temperature-controlled bath at 37 °C. Excess water was removed with absorbent paper. The samples were then blown with N₂ on both sides. The masses were recorded again (m_2). The procedure of placing samples in a desiccator until they reached constant mass (m_3) was repeated. All specimens were measured under controlled temperature and humidity (23 °C, 68%).

For the calculation of sorption and solubility, Equations 3 and 4 were used.

$$Wsp = \left(\frac{m2 - m3}{V} \right) \quad (3)$$

$$Wsl = \left(\frac{m1 - m3}{V} \right) \quad (4)$$

RESULTS

Table 2 shows the results of the properties evaluated of the samples with two different cure protocols.

For the samples cured with CQ were observed low values of degree of conversion compared with lucirin ones. ISO 4049 states 50 MPa as a minimum in flexural strength to dental composites. Can be observed that L-T/p showed the best value among the samples. No significant difference was observed in polymerization shrinkage in samples containing TEGDMA/bis-GMA regardless the photopolymerization system used, and L-T/p showed the best

performance again. All composites have similar and satisfactory sorption and solubility data.

DISCUSSION

For the samples with CQ, high degrees of conversion in both formulations were observed. This fact is probably related to the use of the diluent monomer TEGDMA. A characteristic of this diluent is the high mobility of its chains, causing the undesirable cyclization. This phenomenon produces a high degree of conversion, but it does not reflect an increase in mechanical properties because such bonds occur between same-chain segments or segments of chain already densely crosslinked, leading to microgel domains [15].

Figure 2 shows FTIR graphs of the samples with TEGDMA and p-MEMO.

As described before, Figure 2 shows a larger degree of conversion when lucirin was used. This statement can be related to a more remarkable decrease in C = C peak intensity in Graph (B) when compared with Graph (A). It should be highlighted that baseline corrections were performed before the intensity values were recorded [16]. The same behavior was observed in samples containing the conventional monomers TEGDMA/bis-GMA (plots not shown).

The degrees of conversion for the lucirin-cured composites were superior compared to the CQ-cured samples with the same formulation, Table 2. These data were expected since the photobleaching process of lucirin produces two

Table 2 - Degree of conversion, flexural strength, polymerization shrinkage, sorption and solubility evaluated in cure samples with camphorquinone and lucirin

Composite	DC (%)	FS (Mpa)	PS (%)	Sorption ($\mu\text{g} \cdot \text{mm}^{-3}$)	Solubility ($\mu\text{g} \cdot \text{mm}^{-3}$)
C-T/p	67.33 ± 1.96	44.43 ± 2.86	6.89 ± 1.03	24.62 ± 0.88	4.48 ± 0.90
C-T/B	79.54 ± 0.98	56.44 ± 1.15	4.85 ± 0.81	34.00 ± 0.32	7.12 ± 0.02
L-T/p	80.76 ± 0.78	73.87 ± 1.71	1.08 ± 0.07	24.47 ± 0.57	2.66 ± 0.46
L-T/B	91.97 ± 4.76	34.30 ± 2.31	5.23 ± 0.52	34.67 ± 1.59	5.55 ± 0.34

reactive species and the pyramidal geometry of the phosphonyl radical provides the electron in a more effective way to methacrylate-end polymerization [17,18].

The high values of flexural strength may be indicative of the degree of crosslinks between different segments in the polymer network and thus associated with a better structured three-dimensional network [19,20]. The low values obtained for the samples cured with camphorquinone suggest that the TEGDMA chains do not link different segments in the structure of the polymer matrix due to the cyclization features previously discussed. The flexural strength of the L-T/p composite showed the highest value among all tested formulations. Unlike those observed in the formulations containing camphorquinone, these samples' microgel domains were not being formed due to the ability of lucirin to bind effectively in curing inorganic oligomeric precursors or conventional monomers.

Figure 3 shows the p-MEMO structure.

We suggest that this higher methacrylate group availability of the pMEMO structure compared to bis-GMA led to a lower TEGDMA cyclization ratio in the L-T/p sample.

High polymerization shrinkage values are associated with poor adhesion of the restorations as well as the formation of micro cracks in the composites, which can cause secondary caries [21]. The value of about 5% for the sample C-T/B sample was in agreement with data in literature and can be due to the high amount of TEGDMA [22].

The formation of an inorganic network via siloxane bonds [Si-O-Si] that occurs in the polycondensed p-MEMO suggests lower polymerization shrinkage of the composites due to the pre-existence of an independent three-dimensional network (an intrinsic characteristic of p-MEMO) [23]. However, the C-T/p sample appeared to be contrary to this statement. As explained by Möszner et al., methacrylate groups present in hybrid polymers reduce mobility due to the intrinsic three-dimensional structure of these materials, as the camphorquinone is not suitable for photocuring [24]. Thus, it can be inferred that an even more intense crosslinking occurs with the chains of TEGDMA in a C-T/p composite, which could explain the high value of polymerization shrinkage in this sample. The low polymerization shrinkage presented by the L-T/p sample can be related to the steric hindrance of chains resulting from the inorganic network formed by the siloxane precursor.

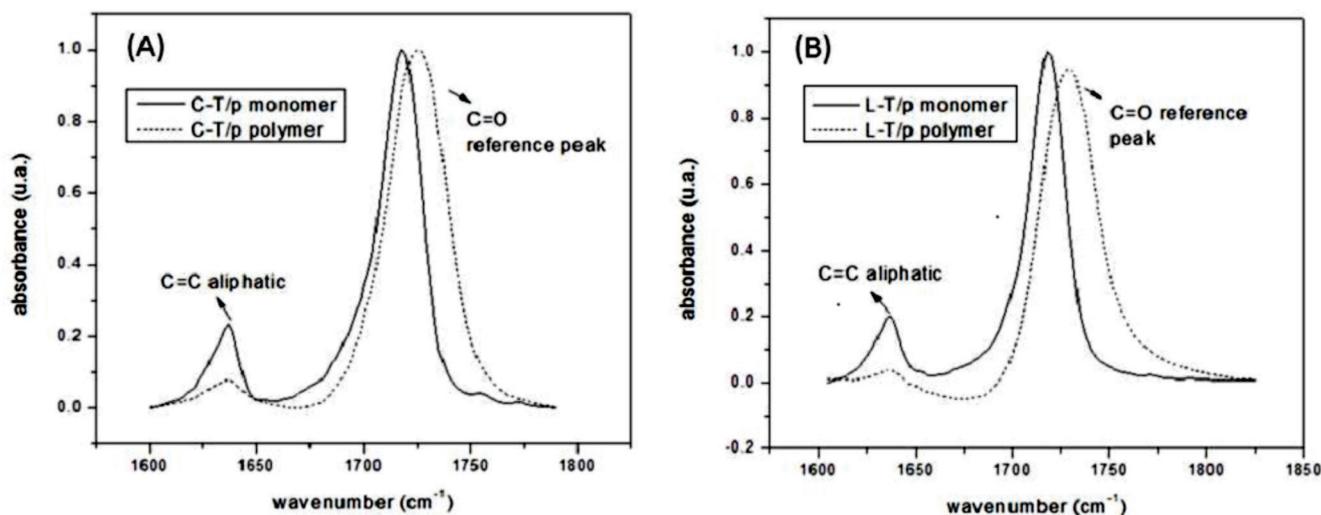


Figure 2 - Infrared spectra of samples containing TEGDMA and p-MEMO before and after curing process. (A) camphorquinone, (B) lucirin.

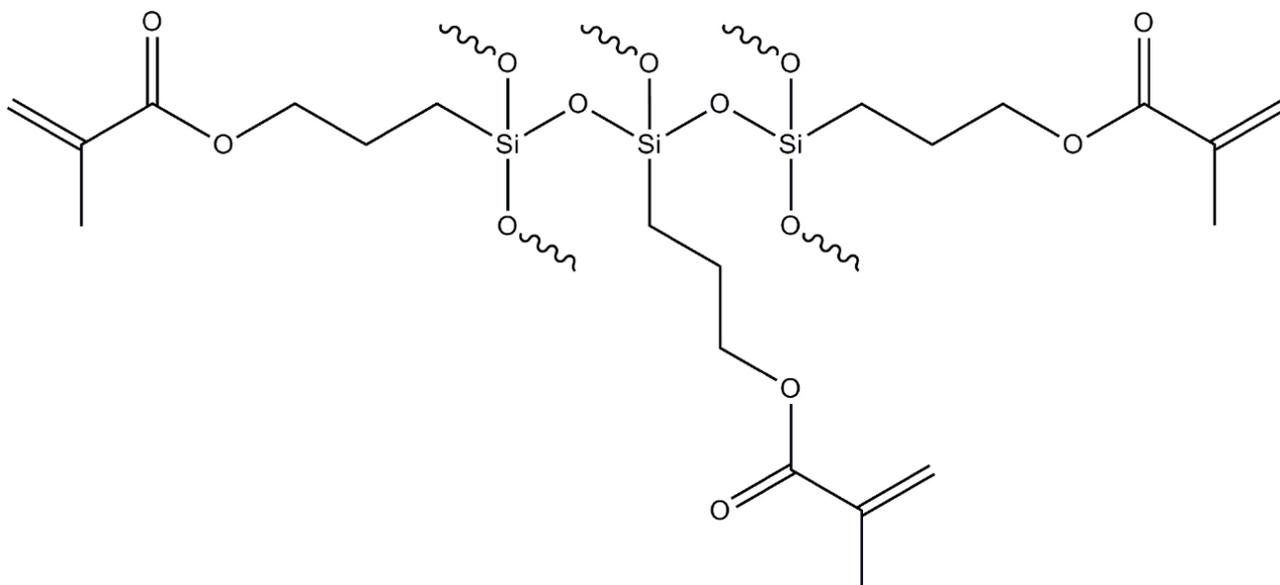


Figure 3 - Chemical structure of the inorganic oligomeric precursor p-MEMO.

As previously discussed, the use of lucirin is not suitable to promote rather polymerization between TEGDMA molecules, thus leading to less-concentrated microgel domains when compared to the camphorquinone-cured sample.

The ISO standard 4049 requires $40 \mu\text{g}.\text{mm}^{-3}$ (sorption) and $7.5 \mu\text{g}.\text{mm}^{-3}$ (solubility) for commercial composites. Due to the three-dimensional oligomeric structure of the inorganic precursor p-MEMO, lower sorption and solubility values were observed in the C-T/p samples. One aspect that may contribute to higher sorption values in the formulation containing bis-GMA (C-T/B) is related to the presence of hydroxyl groups in its structure (Figure 1). Another remarkable issue was the lowest solubility value in the L-T/p sample. This fact may be related to the linkage between TEGDMA and p-MEMO due to the lucirin be a more efficient photocuring system than camphorquinone.

SEM micrographs of cured samples with CQ are shown in Figure 4.

The C-T/p resin showed lower sorption and solubility values when compared to the C-T/B resin. On the other hand, the presence

of cracks provided evidence that the polymeric matrix was being leached during the sorption processes. Because p-MEMO consists of inorganic oligomers of high molecular mass, it could be suggested that the material loss was due to the solubilization of the unreacted TEGDMA monomers or TEGDMA-rich microgel domains. This feature was not observed in the micrographs of composites containing bis-GMA because camphorquinone can bind the chains of these monomers with TEGDMA chains, forming crosslinks.

Comparing the two compositions, sorption tests showed lesser deleterious effects on the sample containing p-MEMO than the composition containing conventional monomers (Table 2). The oligomeric feature of the inorganic hybrid precursor, associated with a more efficient crosslinking by using lucirin, resulted in solubility values below those observed in the CQ-cured samples.

SEM micrographs of the samples cured with lucirin (shown in Figure 5), which presented solubility values lower than those observed in the CQ-cured samples, revealed no cracks in the composite surface. This result

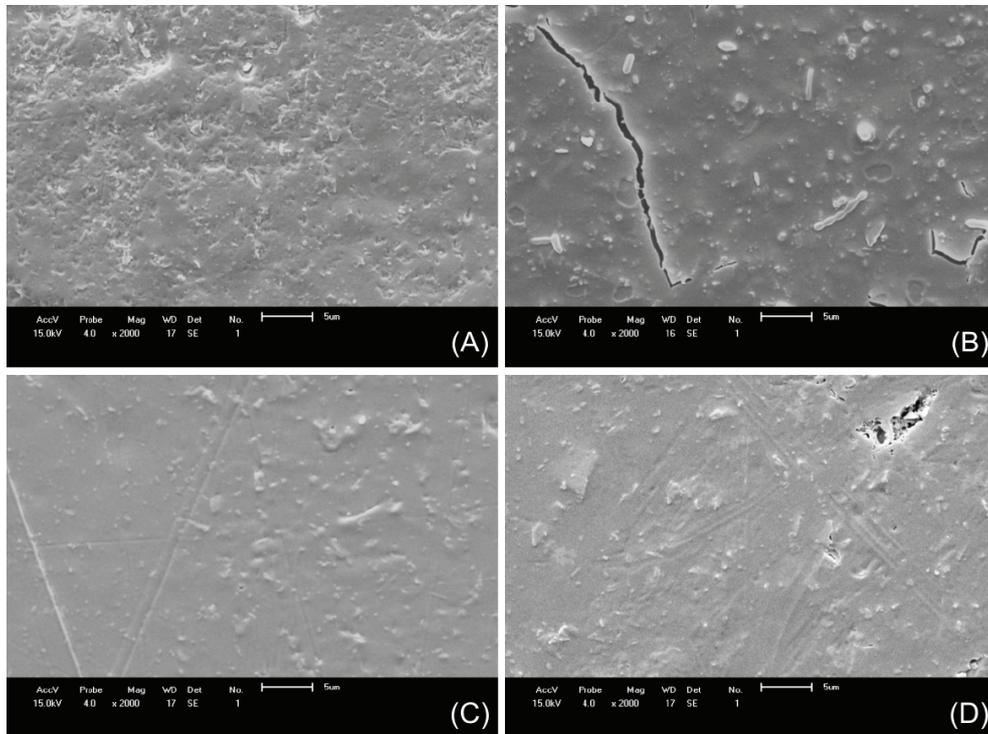


Figure 4 - SEM micrographs (scale 5 µm) of the cured resins with camphorquinone C-T/p (A) before and (B) after of sorption process; C-T/B (C) before and (D) after of sorption process.

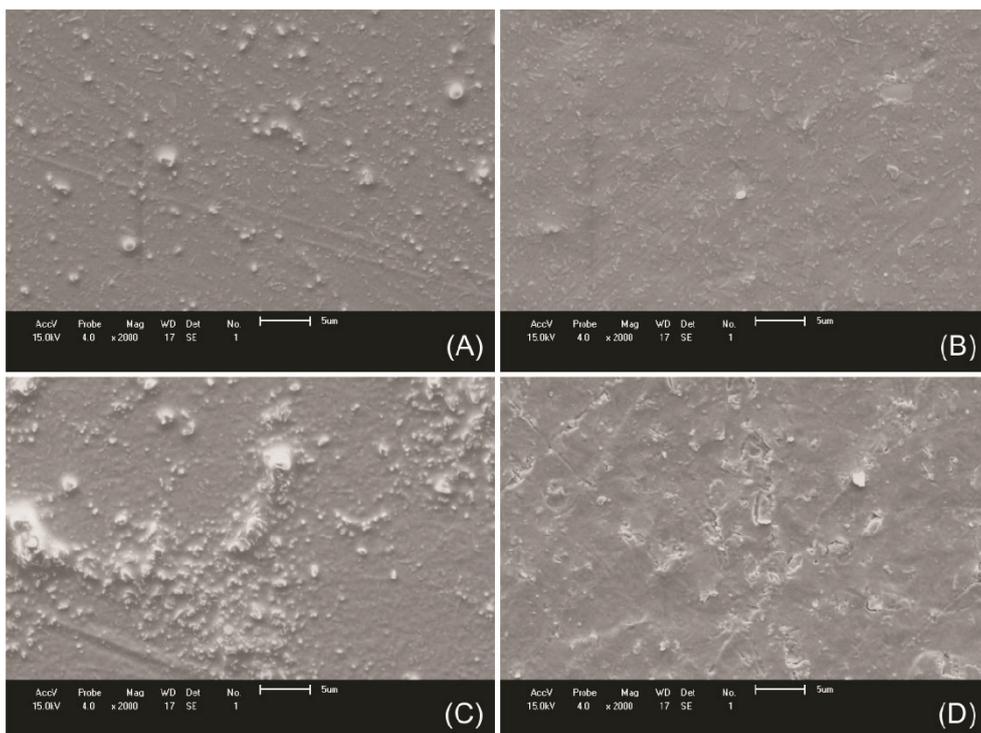


Figure 5 - SEM micrographs (scale 5 µm) of composites cured with lucirin L-T/p (A) before and (B) after of sorption process; L-T/B (C) before and (D) after of sorption process.

suggests a lesser concentration of microgel domains (rich in TEGDMA), showing that lucirin is able to promote crosslinking between chains of p-MEMO and TEGDMA.

CONCLUSIONS

Due to the generation process of free radicals and the geometry of such radicals, one can suggest that the use of lucirin is a more effective photoinitiator in systems containing inorganic oligomeric precursors compared to camphorquinone. The formation of cracks observed in the C-T/p sample may be related to leached unreacted TEGDMA monomers. This suggests that CQ presents lower activity in p MEMO-TEGDMA bonds. When cured with lucirin, samples containing p-MEMO in combination with the diluent monomer showed properties comparable to commercial dental composites. Still, this study suggests further investigations for future development of dental materials with this technology.

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