

Influence of alternative photoinitiators in composite resins: A literature review
Influência de fotoiniciadores alternativos em resinas compostas: Uma revisão da literatura
Influencia de fotoiniciadores alternativos en resinas compuestas: Revisión de la literatura

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Abstract

Objective: To evaluate the influence of alternative photoinitiators present in composite resins related to yellowing, color stability, photosensitivity, light-curing efficiency, degree of conversion, and microhardness. **Materials and methods:** The literature was reviewed by two independent reviewers at PubMed. The search strategy was carried out using the following descriptors: (Photoinitiators, dental) AND (Curing lights, dental) AND (Composite Resins) NOT (Case report). The electronic search was carried out until March 2019, without language restrictions, and inclusion and exclusion criteria were applied in the selection. **Results:** Thirteen articles met the previously established criteria, and all were included. Of these, most were *in vitro* studies. After the aging of the composite, all systems suffered yellowing, however the isolates with camphorquinone were the most affected and, although there is a greater tendency to yellowing, this does not directly affect color stability. However, the literature is still conflicting about which system has significant color stability. Regarding photosensitivity, all photoinitiators have different absorption peaks. In this sense, the photopolymerization must be chosen with caution, as the conversion of monomers and microhardness proved to be directly linked to the correct combination of photoactivator and photopolymerizing unit. **Conclusion:** Alternative photoinitiators have a lower yellowing rate and good color stability. They can be up to five times more sensitive than systems containing isolated camphorquinone. Only third-generation light-emitting diodes photopolymerize satisfactorily composite resins that have alternative photoinitiators in their composition, ensuring a good degree of conversion and acceptable Knoop microhardness values.

Keywords: Composite resins; Curing lights dental; Photoinitiators dental.

Resumo

Objetivo: Avaliar influência de fotoiniciadores alternativos presentes em resinas compostas relacionados ao amarelecimento, estabilidade de cor, fotossensibilidade, eficiência de fotopolimerização, grau de conversão e microdureza. **Materiais e métodos:** A literatura foi revisada por dois revisores independentes no PubMed. A estratégia de busca foi realizada utilizando os seguintes descritores: (Photoinitiators, dental) AND (Curing lights, dental) AND (Composite Resins) NOT (Case report). A busca eletrônica foi efetuada até março de 2019, sem restrições de idioma, e critérios de inclusão e exclusão foram aplicados na seleção. **Resultados:** Treze artigos atenderam aos critérios previamente estabelecidos, e todos foram incluídos. Desses, a maior parte eram estudos *in vitro*. Após o envelhecimento do compósito, todos os sistemas sofreram amarelecimento, porém os isolados com canforoquinona foram os

mais afetados e, embora haja maior tendência ao amarelecimento, isso não afeta diretamente a estabilidade da cor. Porém, a literatura ainda é conflitante sobre qual sistema possui estabilidade de cor significativa. Em relação à fotossensibilidade, todos os fotoiniciadores apresentam picos de absorção diferentes. Nesse sentido, o fotopolimerizador deve ser escolhido com cautela, pois a conversão dos monômeros e a microdureza mostrou-se diretamente ligada à correta combinação de fotoativador e unidade fotopolimerizadora. Conclusão: Fotoiniciadores alternativos apresentam menor taxa de amarelecimento e boa estabilidade de cor. Podem ser até cinco vezes mais sensíveis que os sistemas que contém canforoquinona isolados. Apenas os diodos emissores de luz de terceira geração fotopolimerizam satisfatoriamente as resinas compostas que apresentam fotoiniciadores alternativos em sua composição, garantindo bom grau de conversão e valores de microdureza Knoop aceitáveis.

Palavras-chave: Resinas compostas; Luzes de cura dentária; Fotoiniciadores dentários.

Resumen

Objetivo: Evaluar la influencia de fotoiniciadores alternativos presentes en las resinas compuestas en relación al amarillamiento, estabilidad de color, fotosensibilidad, eficiencia de fotopolimerización, grado de conversión y microdureza. Materiales y métodos: la literatura fue revisada por dos revisores independientes en PubMed. La estrategia de búsqueda se llevó a cabo utilizando los siguientes descriptores: (Fotoiniciadores, dental) Y (Lámparas de polimerización, dental) Y (Resinas compuestas) NOT (Informe de caso). La búsqueda electrónica se realizó hasta marzo de 2019, sin restricciones de idioma, y se aplicaron criterios de inclusión y exclusión en la selección. Resultados: Trece artículos cumplieron con los criterios establecidos. De estos, la mayoría fueron estudios in vitro. Tras el envejecimiento del composite, todos los sistemas sufrieron un amarilleamiento, sin embargo los aislados con canforquinona fueron los más afectados y, aunque existe una mayor tendencia al amarilleo, esto no afecta directamente a la estabilidad del color. Sin embargo, la literatura sigue siendo conflictiva sobre qué sistema tiene una estabilidad de color significativa. En cuanto a la fotosensibilidad, todos los fotoiniciadores tienen diferentes picos de absorción. En este sentido, el fotopolimerizador debe elegirse con cautela, ya que la conversión de monómeros y microdureza demostraron estar directamente ligadas a la correcta combinación de fotoactivador y unidad fotopolimerizante. Conclusión: Los fotoiniciadores alternativos tienen una tasa de amarilleo más baja y una buena estabilidad del color. Pueden ser hasta cinco veces más sensibles que los sistemas que contienen canforquinona aislada. Sólo los diodos emisores

de luz de tercera generación fotopolimerizan satisfactoriamente resinas compuestas que tienen fotoiniciadores alternativos en su composición, lo que garantiza un buen grado de conversión y valores aceptables de microdureza Knoop.

Palabras clave: Resinas compuestas; Luces de curación dental; Fotoiniciadores dentales.

1. Introduction

Self-perception of dental aesthetics has become common in people seeking a harmony relation to the face. The composite resin has become one of the most widely used dental restorative materials, mainly due to its aesthetics similar to dental element. (Vervliet, *et al.* 2018, Shimokawa, *et al.*, 2017)

Most composites have only camphorquinone (CQ) as photoinitiator. CQ has as limitation the yellowing of body resin color due to interaction with tertiary amines into composites (Shimokawa, *et al.*, 2017).

Therefore, manufacturers have been replacing or inserting CQ alternative photoinitiators (AP), such as type I photoinitiators, which means that they do not need a co-initiator molecule to generate free radicals and are capable of generating these radicals from the cleavage of the molecule itself. Examples of this photoinitiators are 1,2-phenylpropanodione (PPD) and acylphosphine oxides: mono-alkylphosphine oxide (MAPO), diphenyl-2,4,6-trimethylbenzoyl phosphine oxide (Lucirin TPO) derived from MAPO, phenylbis(acyl) phosphine oxide BAPO, and 4-propiphenyl-bis (2,6-dichlorobenzoyl) phosphine oxide or also called Igarcure 819. These compounds have white coloration, perfectly suitable to be applied for restore whitening teeth (Vervliet, *et al.* 2018, Oliveira, *et al.*, 2015).

Aiming AP activation, different photoactivators can be used, among them quartz halogen lamp and the light emission diode (LED). The light spectrum emitted by these devices should correspond to the absorption peak of photoinitiator present into restorative material (Shimokawa, *et al.*, 2017, Price, 2017).

The different light absorption peaks of photoinitiators present into composite resins need to be respected to ensure complete polymerization, avoiding interference with mechanical properties (Price, 2017), such as: microhardness, which is crucial to the clinical success, which is directly related to degree of conversion (DC) of the composite. When DC is high it is provided optimum microhardness, but DC is influenced by irradiance and light

spectrum emitted by photoactivator, which should be relative to alternative photoinitiator used (Santini, et al., 2013, Pahlevan, et al., 2016).

Manufacturers are currently inserting more than one photoinitiator into resin composites, forming combined systems, but this specification is not always exposed on the material label. Clinicians could use inappropriate photopolymerization devices and this could interfere negatively properties of composite resins since not all APs are polymerized by blue LED light (Santini, et al., 2013).

Given the above, it was aimed to perform a literature review about the influence of alternative photoinitiators used in composites resins, assessing yellowing and color stability, photosensitivity, photopolymerization efficiency and degree of conversion and microhardness.

2. Materials and Methods

2.1 Search Strategy

An online search was performed by two independent reviewers (NMRA and RVFD) in the PubMed database using as a search strategy with the following descriptors: (Photoinitiators, dental) AND (Curing lights, dental) AND (Composite Resins) NOT case report. The electronic search was performed to march 2019 with no language restrictions.

2.2 Eligibility Criteria and Study Selection

In vitro studies and literature reviews were considered according to the following inclusion criteria: (a) In vitro research using resins composed of the types of photoinitiators explicit in their composition. (b) In vitro research using bovine dental elements for testing; and (c) Research evaluating physical, mechanical and/or other characteristics of composite resins that contained alternative photoinitiators present. Case reports or studies that did not meet the inclusion criteria, were not considered.

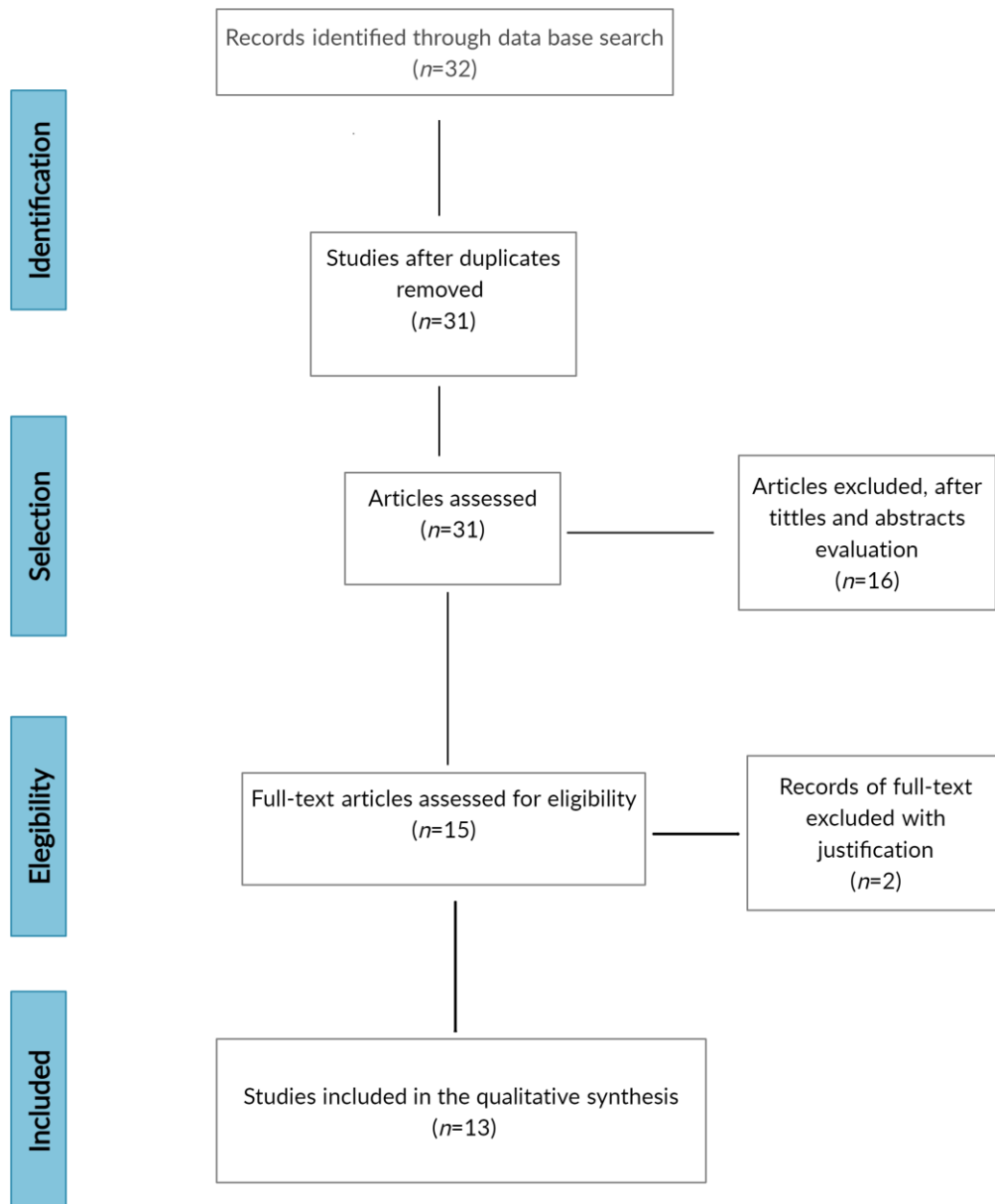
After articles selection, those not directly related to the topic were excluded. Studies that met the inclusion criteria or those with inconclusive information in the title or abstract were selected for full-text evaluation in a second round of this review (Fig. 1).

After inclusion of the studies and evaluation of the full text, the data were recorded in table1.

Studies not included in this review were excluded for the following reasons:

- Experiment with insertion of Lucirin TPO in composite resin aiming only to improve its concentration (Miletic & Santini, 2012).
- The only alternative photoinitiator tested in the study was in a system combined with camphorquinone, so, its results are uncertain for this review (Porto, et al., 2010).

Figure 1. Flowchart of the inclusion criteria of the articles.



Source: Authors (2020).

3. Results

Thirteen articles met the criteria previously established by our study (Table 1). The results are described below.

Table 1. Characteristics of the articles included in this study.

Author/Year	Country	Photoinitiators present in the study	Type of study
Arikawa, et al, 2009	Japan	Camphorquinone, PPD, TPO, Igarcure 819.	<i>In vitro</i>
Brandt, et al, 2011	England	Camphorquinone, PPD	<i>In vitro</i>
Cardoso, et al, 2017	Brazil	TPO	<i>In vitro</i>
Kim, et al, 2013	Japan	PPD, Camphorquinone	<i>In vitro</i>
Miletic & Santini, 2012	England	Camphorquinone, TPO	<i>In vitro</i>
Oliveira, et al, 2015	Brazil	Camphorquinone, TPO, BAPO	<i>In vitro</i>
Oliveira, et al, 2016	Brazil	Camphorquinone and PPD in isolated and combined systems	<i>In vitro</i>

Santini, et al,	England	TPO	<i>In vitro</i>
2012			
Santini, et al,	England	Camphorquinone, BAPO, MAPO, TPO, e PPD	Review
2013			
Schneider, et al,	England	TPO e Camphorquinone.	<i>In vitro</i>
2012			
Silami, et al,	England	Camphorquinone e PPD alone or combined systems	<i>In vitro</i>
2013			
Silva, et al,	India	Camphorquinone e TPO.	<i>In vitro</i>
2011			
Sim, et al, 2012	England	PPD, TPO e Camphorquinone	<i>In vitro</i>

Source: Authors (2020).

3.1 Yellowing and Color Stability

After aging of the composite resin, the yellowing rate over time is higher in any light curing system. But, isolated camphorquinone (CQ) systems are the most affected, thus turning yellow when compared to type I systems containing phenylpropanoldione (PPD), Lucerin TPO, or BAPO which are alternative photoinitiators that already have a lighter color, or combined systems with PPD and CQ and TPO + CQ when cured with the same LED unit (Silami, et al. 2013, Oliveira, et al., 2015).

However, color stability over time is higher in composites with camphorquinone, although it has a higher tendency to yellowing. This does not directly affect the color stability of composites which use CQ as the main alternative photoinitiator (Silva, et al., 2011).

However, there is some disagreement in literature, since according to Arikawa et al. (2009) TPO has greater stability than CQ.

3.2 Photosensitivity

Photoinitiators do not have the same sensitivity (absorption peaks are different) and lucirin TPO is five times more sensitive than systems using camphorquinone (Santini, et al., 2013).

Camphorquinone is sensitized by blue light spectrum (420-540nm), whereas compounds containing only TPO and PPD use violet light spectrum (360-420 nm). However, when CQ is associated with TPO or PPD they can be sensitized with both spectra (Santini, et al., 2013, Silami, et al., 2013). However, when these alternative photoinitiators are subjected only to the narrow blue band spectrum, the expected sensitization does not occur, in other words, the light curing was not completely achieved (Schneider, et al., 2012, Silami, et al., 2013, Cardoso, et al., 2017).

3.3 Light Curing Efficiency

The curing efficiency is directly linked to the type of curing unit used. The most commonly used units are the 2nd and 3rd generation Light Emission Diodes (LED), and halogen lamps can also be found in the market (Brandt, et al., 2011).

The 3rd generation LEDs provide optimal polymerization into resins containing Lucirin TPO, PPD, BAPO, and other alternative FTIs, while second generation and halogen lamps have been found to be ineffective, being more effective in compounds with CQ (Alvim, et al., 2007, Shortall, et al., 2012, Silami, et al., 2013, Oliveira, et al., 2015).

3.4 Degree of Conversion and Microhardness

Among the studies presented in this review conversion of monomers into polymers (and consequently microhardness) showed to be directly related to an appropriate sensitization of photoinitiator (s) and consequently a correct combination of photoactivator and photopolymerization unit (Sim, et al., 2012).

When cured with halogen lamps, photoinitiators such as PPD have degree of conversion and Knoop microhardness values reduced, when compared with when

photopolymerized by third generation LEDs (Sim, et al., 2012). Third generation LED units (Polywave) ensure a better degree of conversion and microhardness in composites containing TPO, PPD, as well as those containing camphorquinone (Miletic & Santini, 2012, Santini, et al., 2012, Kim, et al. 2013).

4. Discussion

Acylphosphine oxide-derived compounds, such as TPO, BAPO and MAPO, have been suggested as substitutes for camphorquinone in composite resins to reduce yellowish effect (Rueggeberg, 2011) mainly in composites for bleached teeth. Unlike conventional composites, which use CQ as major photo-initiator, TPO, BAPO and MAPO based resins do not require a co-initiator (usually tertiary amines) to initiate the polymerization. This potentially reduce yellowing effect caused by the oxidation of tertiary amines into composites for bleached teeth (Schroeder & Vallo, 2007). It is known that amines will form byproducts from their photo decomposition, causing discoloration with a tendency of yellow to red/brown color under the action of light or heat (Alvim, et al., 2007, Llie & Hickel, 2008) So TPO, BAPO and MAPO based composites acquire higher color stability compared to conventionals (Silva, et al., 2011).

Photoinitiators type I (alternatives) have a unidirectional cleavage reaction, do not require co-initiator thus ensuring their lighter color and are sensitive to UV rays. When their polymerization is not completed, unreacted molecules are retained in the polymer matrix and are still capable of being cleaved when exposed to UV light again (Alvim, et al., 2007, Llie & Hickel, 2008). Nevertheless, since the molecular mobility of radicals is greatly obstructed in the polymerized polymer, they can remain trapped within the structure without contributing to further polymerization, although they may result in color change of composite, which would explain decreased color stability in these photoinitiators (Oliveira, et al., 2015).

However, the yellow effect caused by non-photopolymerized alternative photoinitiator is also related to their concentration in compounds. According to Schneider *et al.* (2012), the effect of yellowing proportionally increases with alternative photoinitiator concentration increases into composite resins.

On the other hand, even that yellowing promoted by incorporation of camphoroquinone is not considered critical when the composite has a dark shade, in composites for bleached teeth, this is a significant factor. A smaller amount of CQ is added

to avoid this intrinsic yellow color, avoiding compromises clinical materials properties (Shortall, et al., 2012) and still influence light curing (Schneider, et al, 2016).

For this reason, it is important to note that inadequate polymerization may decrease mechanical and physical properties into composites with only CQ (conventional) or CQ and alternative photoinitiators (composites for bleached teeth), leading to cavity retention failures, increased solubility, presence of marginal infiltration and pulp response to unpolymerized monomers. Each photoinitiator has a particular absorption spectrum, sensitive to certain wavelengths. Therefore, for the activation of the photoinitiators, the light curing devices must emit radiation near their absorption peak. If emission and/or absorption capacity are not compatible, then little or no polymerization will occur (Shortall, et al., 2012, Schneider, et al., 2016).

Camphorquinone is a photoinitiator which is photoactivated when exposed to wave length of 468nm (Brandt, et al., 2011). MAPO, BAPO and phenylpropanedione need wave length of 381, 371, and 410nm, respectively to be activated, and only a portion of their absorption ranges are within the visible light spectrum (Shortall, et al., 2012, Lee, et al., 2012). So, alternative photoinitiators are better light cured by violet light range, that is, they do not have good polymerization with halogen lamps or 1st and 2nd generation LEDs. Thus, the 3rd generation Light Emission Diodes (LEDs), in addition to the emission of blue light, also carry the emission of violet light color range, capable of adequately light cure the alternative photoinitiators (Alvim, et al., 2007). Thus 3rd generation LEDs are the best clinical choice for composites for bleached teeth.

Finally, degree of conversion and microhardness are closely linked to light curing. If the photoactivator unit does not emit sufficient light at wave lengths that are absorbed by the photoinitiator, then the polymerization rate may be inefficient (Neumann, et al., 2006, Brandt, et al., 2010). Thus, the monomer-polymer conversion and material microhardness are significantly reduced causing a relatively inferior material in terms of physical and mechanical characteristics. This is an important clinical factor to be observed for the correct choice of resin type (and inherent photoinitiator type), and an appropriate photocuring unit to be used.

5. Conclusion

Alternative photoinitiators (AP) have a lower yellowing rate when compared to isolated systems with only camphorquinone (QC) in the composition. However, color stability

is still a point of discussion. APs have different photosensitivity (absorption peaks), which can be up to five times more sensitive than isolated QC systems, for this reason only third generation light-emitting diodes correctly light-cure composites containing a significant amount of these photoinitiators in its composition, guaranteeing a good degree of conversion and acceptable Knoop microhardness values.

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