



Effects of photoinitiators on dental composite resins: a narrative review

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Abstract

In recent years, the components of dental composites have changed in an attempt to improve their biomechanical and chemical properties. Therefore, dentistry contains many different photoinitiator systems, the most common being the binary camphorquinone and tertiary amine system, and most dental light curing agents are designed to suit the camphorquinone (CQ) absorption range. The alternation of the photoinitiator can cause changes in the values of biomechanical properties, such as degree of conversion, hardness, and biocompatibility. This review contains a comparison of the biomechanical properties of dental composites including different photosensitizers, among others: camphorquinone, phenanthrenequinone, benzophenone, and 1-phenyl-1,2 propanedione, trimethyl benzoyl-diphenylphosphine oxide, benzoyl peroxide. The literature reviews used and the observation of randomized studies were from the Bireme, PubMed, SciELO, and LILACS databases from 2008 to February 2021. Objective: To present the action of light-curing agents in composite resin and their mechanical characteristics concluded that the market is constantly evolving related to photoinitiators.

Keywords: Photoinitiators. Composite Resin. Dentistry.

Introduction

Organic dental composite resin formulations include photoinitiation systems that absorb light and drive the molecules to excited states and from there free radicals or other initiator species form and initiate the conversion of oligomer mixtures into a cross-linked polymeric network [1]. Nassar et al. [2] explain that polymerization shrinkage is an inherent property of the

composite resin and occurs when the monomer is converted into a polymer, this phenomenon is still considered a disadvantage of the composite resin, as it has a great impact on its clinical performance.

Camphorquinone (CQ) is the most widely and successfully used photoinitiator in dental resin materials. Despite their high clinical acceptance, CQ-based photoinitiator systems are responsible for a yellowish color in resin-based materials [3]. Therefore, a lot of focus has been given to the so-called nanotechnology, which consists of the manipulation and measurement of materials on a scale of below 100 nanometers, these new materials have inorganic particles ranging from 20 to 75 nm, which reduces the polymerization contraction and promotes a smooth surface. quite satisfactory [4].

Because of this, common dental composites are cured by light activation, this is possible due to the presence of the light-curing initiator system and their amounts vary from 0.1% to 1% by weight, whereby the amount of the initiator depends on the type of photosensitizer. and the optimal concentrations of initiators in resin-based composites depend on many factors such as solubility of these compounds in the monomer, photoreactivity, color, or biocompatibility [5].

Results

Development

Evolution and Properties of Dental Composites

This process began in 1955 when Michael Buonocore discovered a simple method of increasing the adhesion of acrylic restorations to enamel using orthophosphoric acid. The second step was the discovery of Dr. Bowen: Bisphenol A-glycidyl methacrylate (Bis-GMA resin), which has been a basic

compound of dental composites since 1960. In 1975, for the first time, dental resin composite was light-cured. The change in the curing of dental composites eliminated the porosity of the composite and allowed the dentist to control the application of the material in the dental cavity, so dentistry took a big step that day, but there was still progress to be made [5].

Composite dental restorations were first introduced to the field of restorative dentistry in the 1960s. Despite more than 50 years of development, the durability of composite resin restorations is still not equal to that of traditional amalgam restorations [6]. Kowalska et al [5] explain that the properties of dental composites are divided into three groups, where the first group includes: strength, rigidity, abrasion resistance, and thermal expansion coefficient.

All three components of the compound: filler, matrix, and coupling agent, are responsible for these characteristics, the softening tendency and color stability are in the second group and are caused by the type of matrix and photoinitiator. The last group contains polymerization shrinkage and water sorption which is mainly connected with the matrix type [5].

Composite Resin Polymerization Shrinkage

The polymerization shrinkage is still considered a disadvantage of the composite resin as it has a great impact on its clinical performance, this phenomenon is due to the decrease in the distance between the monomer molecules caused by the formation of covalent bonds as the polymerization reaction occurs [2].

Yet Nassar et al. [2] explain that to prevent premature polymerization small amounts of butylhydroxytoluene (BHT; approximately 0.01% by weight) are normally used as an inhibitor, this ingredient is also important to increase the shelf life of the resin during its storage and transport.

Incomplete polymerization can compromise the performance of resin-based dental restorations. The presence of residual monomer can have a plasticizing effect on the polymer, thus altering the physical and mechanical properties of the hardened materials. Furthermore, the presence of unreacted monomer can make the polymer matrix more susceptible to oxidative and hydrolytic degradation reactions, leading to lower durability, it is therefore important to evaluate the final degree of conversion of the monomer into polymer after polymerization [7].

Functioning of Photoinitiators

In dental resins, photopolymerization is catalyzed

by mixed photoinitiator systems and takes place in the moist environment of the mouth. The model resin formulations used are a mixture of a hydrophobic component (bis GMA) and a hydrophilic component (HEMA) and are based on conventional dentin adhesives. Commercial adhesives were not used, as differences in filler type and content, additives, and processing conditions between different manufacturers can influence the results and adversely affect reproducibility [7].

Appropriate combinations of light sources, exposure time, and photosensitizer or co-initiator systems are considered key factors in optimizing the photopolymerization of dental composites because improved conversion is critical for optimizing mechanical properties, and clinical performance, longevity, and biocompatibility [1].

Recently, the APS (Advanced Polymerization System) was launched on the market, which consists of a combination of different photoinitiators that interact with each other, increasing the activation capacity of the light emitted by the photopolymerization units. Added to different materials, the system offers several advantages and the main benefit is the increase in the degree of conversion in the hybrid layer, which increases the bond strength and consequently the mechanical properties of the adhesive film (greater cohesive strength) another advantage is the absence of color in this system, avoiding any kind of interference in the performance of restorations and cementation in anterior teeth [8].

Jäger et al. [9] explain that the traditional photoinitiator system, which includes camphorquinone and a tertiary amine (CQ/amine), has some disadvantages: CQ absorbs light with a wavelength between 400 and 500 nm, with a maximum absorption peak in the visible range. at 468 nm. It presents an intense yellow color and requires a co-initiator molecule to optimize the polymerization reaction, which unfortunately can undergo oxidation with time, leading to greater intrinsic discoloration, in addition, in acid CQ medium it shows limited regeneration.

Alternative photoinitiator systems have been suggested to replace CQ in dental materials to reduce this yellowing effect, especially in resin-based materials for whitened teeth. On the other hand, alternative photoinitiator systems for resin materials must not only have an acceptable initial and long-term aesthetic appearance, but also adequate mechanical properties [3].

Phenylpropanedione (PPD) is suggested as an effective alternative photoinitiator to reduce this yellowing. As a Norrish Type I photoinitiator, PPD reacts

by photolysis in which the cleavage of the CC bond between the carbonyl functional groups of its molecule leads to the formation of free radicals initiating polymerization. However, PPD can also react via a co-initiator as it has the same diketone group as camphorquinone. Thus, the radicals derived from the amine-based H transfer co-initiator are responsible for initiating polymerization [3].

Kowalska et al. [5] explain that there are two types of photoinitiators: 1 type is trimethyl benzoyl-diphenylphosphine oxide (TPO), benzoyl peroxide (BPO), and type 2 is camphorquinone (CQ), phenanthrenequinone (PQ), benzophenone (BP) and 1-phenyl-1,2 propanedione (PPD) which combined two forms of polymerization:

• Type 1 Photoinitiators

Norrish type 1 photoinitiators improve the properties of materials in dental composites, they have low energy bonds that after homolytic cleavage produce more active radicals and allow photopolymerization by shorter wavelength and higher energy photon of violet light. Type 1 photosensitizers increase curing efficiency due to higher molar absorptivity. Another advantage of these primers is the improvement of tissue color matching as a result of low pigmentation due to absorption of the shorter wavelength range. The ultimate benefit is reduced elution of residual monomers that increase the crosslink density of the resin. These photosensitizers do not require co-initiators and their color is not as yellow as type 2 photoinitiators, but after polymerization, they turn yellow due to the high concentration of residual monomers [5].

• Type 2 Photoinitiators

Type 2 photoinitiators are, for example, CQ, PQ, and BP with co-initiators, and their absorption band is between 400–490 nm. Initiation is generally slower than photoinitiation caused by type 1 sensitizers because it is based on a bimolecular reaction. Polymerization is initiated by visible blue light photons. CQ co-initiators are primarily aromatic tertiary amines. The concentration of CQ and co-initiators is obtained to obtain a high degree of conversion since the polymerization is initiated by the irradiation of blue light by the carbonyl group of CQ and the transition to a triplet state using excitation to a single state. The formation of the radical is highly dependent on the type of co-initiator, the concentration, and its structure. This type of photoinitiator is more useful than the Norrish type due to better optical absorption properties in the near-visible wavelength region [5].

Kowalska et al. [5] say that during the search for the middle ground, many experimental photosensitizers

were discovered, for which the most promising is the germanium compounds. They are soluble in most monomers and have greater photocuring activity than CQ. Another benefit of BTMGe and DBDEGe is the absorption range, which approaches CQ and therefore does not require different curing units.

Types of Composite Resins

Composite resins are esthetic restorative materials commonly used in dental clinics [10], Trevisan et al. [11] state that it is currently a material of choice for direct anterior and posterior restorations due to its ease of handling, preservation of dental tissue, structural reinforcement, adhesion, low cost and especially the natural appearance of these materials. With the constant evolution of dental materials, conservative treatment has become increasingly viable, mainly because it offers advantages such as dental preservation, less working time, low cost (when compared to ceramic), and providing aesthetic results as satisfactory as [12].

Today, there are several types of resins in the markets, which differ in their composition, which emerged during this evolutionary process, each having its indications and limitations [4]. Among the composite materials currently available, hybrid, microfilm, and nanoparticulate composites are commonly used for posterior restorations. Micro-filled composites have a filler of 37%–40% by volume, while nano-filled composites have a filler of 60% by volume. Nanoparticulate composites show high translucency similar to microfilm composites and physical properties similar to hybrid composites. In addition to being aesthetic, these materials are relatively cheaper, induce less wear on the opposing tooth structure, and are based on the principle of a minimally invasive procedure [13].

• Macroparticle Resins

Macroparticle resins practically no longer exist since, due to the size of the inorganic particles, they presented unsatisfactory surface smoothness [4]. Because they present inorganic particles and variation in particle sizes that vary between 8 and 12 micrometers, their main clinical characteristic is high roughness and difficulty in polishing, thus promoting unsatisfactory aesthetic results [14].

• Microparticle Resins

The microparticulate resins, despite having excellent polishing, have the disadvantage of a high rate of polymerization shrinkage due to the low percentage

of filler by weight of these resins. Nowadays they are indicated for the application of a surface layer in the esthetic restorations of anterior teeth [4,14].

Hybrid and Microhybrid Resins

To combine the advantages of macro and micro-particle resins, hybrid and micro-hybrid resins have emerged ranging from 0.6 and 1.0 micrometers, which currently represent the largest contingent of commercial brands, and according to the manufacturers, they have a “universal” indication”, which can be associated to obtain better results with better mechanical resistance, excellent polishing capacity and surface maintenance [4,14].

Nanoparticulate and Nano-hybrid Resins

Then came the nanoparticulate and nano-hybrid resins, with variations between particles of 5 and 75 nanometers, that is, smaller particles that help in the high standard of polishing and consequent superior aesthetics, standing out with an excellent polishing, greater longevity, smooth surface, and high mechanical resistance, presenting less wear of the restorations [14].

Flow and Compactable resins

Composites can also differ concerning their flow, there are today the so-called flow and packable resins. The first has high fluidity and is indicated for ultra-conservative cavities and as a lining in restorations of posterior teeth to function as a shock absorber due to the low modulus of elasticity [4].

Bulk Fill Resins

Bulk-fill resins were developed as an alternative to conventional resins, inserted in increments of up to 2 mm, as the bulk-fill variety presents effective light curing in increments of up to 4 mm. These 4 mm increments have caught the attention of pediatric professionals in their dental practice due to the shorter clinical time associated with reduced shrinkage. When used in routine practice, bulk-fill resins have advantages over conventional resins, due to their reduced and uncompromised clinical time, such as polymerization shrinkage [15].

Bioactive Resins

Bioactive glass (BAG), first introduced in the early 1970s by Hench and his co-workers, is capable of forming direct chemical bonds with both hard and soft tissues. The SACO contains oxides of calcium, sodium,

phosphorus, and silicon in a proportion that gives the material exceptional surface activity, interest in potential dental applications of particulate BAG has expanded in recent years due to its biocompatible nature and the potential remineralizing effect of BAG, based on the release of calcium and phosphate ions, has also attracted much attention [16].

It has been shown that bioactive glass fillers can be successfully incorporated into dental resin composites to induce bioactivity, ie calcium phosphate precipitation, and exert antimicrobial effects at dental-restorative interfaces [9].

Resin with S-PRG remineralizing capacity

Recently, a nanohybrid composite resin with pre-reactive glass surface ionomer cement (S-PRG) promises to release and absorb the fluoride in the oral environment [17]. And Kowalska et al. [5] explain that the S-PRG eluate has antibacterial activity and inhibits the formation of oral biofilm. Resin composites consist of three different materials: an organic phase (matrix), a dispersed phase (inorganic filler), and an interfacial phase (coupling agent to bond the filler to the organic resin) [18].

The filler is known to suppress thermal expansion and polymerization shrinkage of resin composites, as well as to provide fracture resistance. Surface pre-reacted glass ionomer (S-PRG) fillers are prepared by an acid reaction between fluoro-boron-aluminosilicate glass and polyacrylic acid solution [18].

Shiyya et al. [19] agree that the surface pre-reacted glass ionomer (S-PRG) filler releases various ions including fluorine, strontium, sodium, boron, aluminum, and silicate ions, a further account that in particular fluoride and strontium ions released by S-PRG filling can change the hydroxyapatite in dentin to fluoridated apatite, fluorapatite or strontium apatite during demineralization and remineralization. Fluoride released by the S-PRG filler likely induces fluoroapatite-like precipitation in lesion bodies, inhibiting further demineralization [19].

Fluoride and strontium ions are released from the S-PRG filler containing temporary filler materials and react with hydroxyapatite to form fluorapatite, strontium apatite, and/or fluoride apatite. Strontium ion was also involved in the caries dentin remineralization process, and the remineralization effect was affected by the concentration of fluoride ions when used together with them [19]. Furthermore, boron, silicon, and strontium ions can promote bone formation by inducing osteoblastic differentiation of mesenchymal cells [18].

Discussion

The composition of the composite resin is closely related to satisfactory physical and mechanical properties, so the type and size of the charged particles, the type of monomer present in the resin matrix, the concentration and/or type of activators, initiators, and inhibitors, and even camphorquinone (CQ) after polymerization can interfere with the quality of the material [8].

Park et al. [7] says that the chemistry of the photoinitiators used in dental resins is critical for their efficient polymerization and the satisfactory mechanical and physical properties of the polymer and that most photoinitiators formulated for commercial dental resins consist of two components, where, the photoinitiator (usually a camphorquinone, CQ) which can absorb light directly and a co-initiator (usually an amine) which does not absorb light but interacts with the activated photoinitiator to generate a reactive free radical and initiate polymerization.

The depth of polymerization and CQ are closely linked to the ability of light to penetrate the composite resin, which is determined by its translucency and the presence and type of filler. Thus, the characteristics of the inorganic matrix in dental composites have a great impact on the polymeric conversion of these materials. The type, size, and concentration of the charge can considerably affect the ability of light to be transmitted through the composite resin layer [8].

Park et al. [7] agree that CQ is a typical visible light-activated free-radical photoinitiator with an absorbance range between 400 and 500 nm. CQ requires a tertiary amine reducing agent, usually ethyl-4-(dimethylamino)benzoate (EDMAB) and or 2-(dimethylamino)ethyl methacrylate (DMAEMA), for efficient polymerization to occur, three-component systems, in which an Iodonium salt is added to the above two-component systems, have recently emerged as efficient and visible light sensitive photoinitiators. Nassar et al. [2] says that the systematic investigation of the interaction of the various components in the initiator system provides a starting point for understanding the impact of the initiator system on the polymerization kinetics of the polymer.

Shin et al. [1] also agree that CQ has been used as a photoinitiator most commonly in dental composites because it has a maximum light absorption at 468 nm which combines well with conventional dental curing lamps. However, it has some disadvantages such as low polymerization efficiency and toxicity. Photolysis of a diketone leads to the homolytic cleavage of the CQ bond between the two carbonyl groups, resulting in two carbonyl radicals. This radical pair can escape the cage

to form photodecomposed products. However, the two carbonyl radicals in CQ are structurally linked to each other and the probability of their recombination in CQ is high. The consequent low efficiency of CQ polymerization results in relatively low mechanical properties without relatively high concentrations of CQ and/or relatively long exposure times, as well as possible toxic effects from residual unreacted monomers.

OPPI has been used as an additional or alternative photoinitiator to increase the degree and rate of conversion and, in addition, to overcome the color problems associated with CQ. It was observed that the optimal concentration of photosensitizer/co-initiator depends on many factors, such as solubility of these compounds in the monomer mixture, absorption characteristics of the sensitizer, photoreactivity (ability to form free radicals when the photosensitizer and co-initiator react), the effects of these compounds on color, the overlap between the wavelengths of emission from the light source and absorption of the photosensitizer, and the biocompatibility of the components in the photoinitiator system [1].

For Park et al. [7], the studies reported here showed dramatic differences in DC and CT of bis GMA resin, HEMA between two-component (CQ/DMAEMA and CQ/EDMAB) and three-component (CQ/DMAEMA/DPIHP and CQ/EDMAB/ DPIHP). Furthermore, the resin formulated with the aliphatic amine (i.e. DMAEMA) had significantly ($p < 0.05$) lower DC and longer TC than the resin formulated with the aromatic amine (i.e. EDMAB), especially in the presence of water. This result is in agreement with previous findings that demonstrated a faster polymerization rate and higher DC with the CQ/aromatic amine initiator system. The addition of DPIHP to two-component initiator systems increased DC and dramatically reduced TC [7].

Nowadays, in dentistry, there are many different photoinitiator systems, the most common is the binary camphorquinone and tertiary amine system, and most dental light curing agents are created to suit the absorption range of CQ. However, CQ has not been the best solution because of the yellow shading caused by the yellow color of CQ and the coloring connected with amines. The first type 2 photoinitiator used in the industry was the BP. CQ is most effective in dentistry, but BP is still used, for example, in 3D printing. Furthermore, BP with its co-initiators can be used with CQ and this combination improves the properties of the dental resin [5].

Thus, Kowalska et al. [5] report that in recent years new acyl phosphine oxide photoinitiators were invented, namely 9-(2,4,4,6-trimethyl benzoyl)-9-oxytocin-9-phosphate-fluorene (TMBOFP) and 9-(p-toluy)-9-

oxytocin-9-phosphfluorene (TOPF) these new photosensitizers have greater photopolymerization reactivity in visible and ultraviolet light. Its light-curing reactivity is comparable to that of BAPO. Benzoyl germanium substances - BTMGe and DBDEGe are new visible light photoinitiators in dentistry, the photolysis of mono-germyl ketones in cyclohexane solution was described 15–20 years ago, whereby this process generates two radicals: benzoyl and germyl Benzoyltrimethylgerman (BTMGe) is a yellow liquid and dibenzoyl-diethyl german (DBDEGe) is a yellow solid and the maximum absorption absorbance of BTMGe is 411 nm and of DBDEGe is 418 nm.

Some authors agree that more studies are needed as it is a big problem to discover the golden medium that connects the proper mechanical properties and the esthetic appearance of the restoration.

Conclusion

It can be concluded from this literature review that the photoinitiator system branch is still under development and a small part of the composition of dental composites has a great influence on the biomechanical and chemical properties of the materials. However, it is necessary, but studies referring to new technologies to assess the effectiveness and appropriate mechanical properties apply to composite resin and the esthetic appearance of the restoration.

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