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Dr. Shweta Singh
Post Graduate Student,
Department of Conservative
Dentistry & Endodontics, Babu
Banarasi Das College of Dental
Sciences, BBD University,
Lucknow, India

Dr. B Rajkumar
Professor & Head, Department
of Conservative Dentistry
& Endodontics, Babu Banarasi
Das College of Dental Sciences,
BBD University, Lucknow,
India

Dr. Vishesh Gupta
Associate Professor, Department
of Conservative Dentistry
& Endodontics, Babu Banarasi
Das College of Dental Sciences,
BBD University, Lucknow,
India

Dr. Akanksha Bhatt
Assistant Professor, Department
of Conservative Dentistry
& Endodontics, Babu Banarasi
Das College of Dental Sciences,
BBD University, Lucknow,
India

Correspondence

Dr. Shweta Singh
Post Graduate Student,
Department of Conservative
Dentistry & Endodontics, Babu
Banarasi Das College of Dental
Sciences, BBD University,
Lucknow, India

Current photo-initiators in dental materials

Dr. Shweta Singh, Dr. B Rajkumar, Dr. Vishesh Gupta, Dr. Akanksha Bhatt

Abstract

Light induced reactions are based on the absorption of light that excites the electrons of a molecule and can, under favorable circumstances, lead to dissociation, isomerization, abstraction, electron or energy transfer, and bond formation. The most commonly used initiating system for photopolymerizable dental implants is a Type II PI consisting of camphorquinone (CQ) and ethyl 4-dimethylaminobenzoate (DMAB). However, this bimolecular PI-system exhibits numerous significant drawbacks such as low reactivity and stability, especially in water-based formulations. The demand for an appropriate PI for visible light curing is high for dental restoratives. This paper reviews the options of new photoinitiators for restorative materials.

Keywords: Photoinitiators, Photopolymerisation, initiator, co-initiator, Camphorquinone, Phosphine oxides

1. Introduction

In dental composites, monomers are polymerized by light with the presence of photoinitiators (PI). Free-radicals, which promote polymerizations of vinyl monomers, are formed when PIs are excited by irradiation (either UV or visible light). Free radical photopolymerization (FRP) is undoubtedly the most popular compared to cationic photopolymerization (CP). Upon excitation, in FRP, PI becomes excited (PI*) and generates a radical, R, either directly through cleavage or in the presence of an electron/hydrogen donor. In CP, onium salts (e.g., the iodonium salt) are used as PI. Their direct homolytic/heterolytic decomposition followed by hydrogen transfer reactions leads to a proton. Their photosensitized decomposition occurs according to energy or electron transfer. The PI, PS and RS have to be selected to absorb the irradiation wavelengths of near UV/visible photosensitive systems for FRP. In CP, the PIs mainly absorb in the UV. Accordingly, we differentiate between UV, VL and NIR photoinitiators, which absorb light in the respective spectral region. As the light energy is inversely proportional to the wavelength, ultraviolet light has more energy than visible light or NIR radiation. The radicals that initiate the polymerization reaction are either formed by means of bond fission or by the transfer of a hydrogen atom H from a second compound, the so-called coinitiator. Irrespective of the mechanism used, it is important that the photoinitiator reaches an excited state due to the light energy absorbed.

2. Mechanism of Photoinitiated Radical Polymerization

Photoinitiated radical polymerization may be initiated by both cleavage (type I) and H-abstraction type (type II) initiators. The radical generation processes of type I and type II photoinitiators are entirely different. While type I photoinitiators generate initiating radicals by a unimolecular cleavage reaction, type II initiators undergo bimolecular hydrogen abstraction reactions. The main cleavable photoinitiators include benzil dimethyl ketal, benzoin ethers, alkyl hydroxyphenyl ketones, dialkoxyacetophenones, benzylcyclohexanol, amino alkyl ketones, acylphosphine oxides and acyl germanes. Except for acylphosphine oxide and acylgermane photoinitiators, the cleavage takes place at carbon-carbon bond. Long wavelength and visible light active acylphosphine oxide and acylgermane photoinitiators undergo cleavage at carbon-phosphorous and carbon-germane bonds upon irradiation, respectively [1, 2].

3. Camphorquinone

The photoinitiator absorbs light, and is promoted to an excited state that interacts with a photo reducer (electron or proton donor molecule) to initiate a free radical addition polymerization of the resin monomers. Camphorquinone (CQ), a blue light photoinitiator, is commonly used in dental resin formulations. CQ is di-2, 3-diketo-1, 7, 7-trimethylnorcamphane with molecular weight of 166.2 and has an absorption peak around 469nm. CQ is a 'Type II' photoinitiator (i.e., H-abstraction) where, upon photoexcitation, it abstracts a hydrogen from the tertiary amine H-donor to yield a reactive, initiating radical centered on the amine and a relatively unreactive camphorquinone-centered radical [3]. As hydrogen abstraction only proceeds while the Type II photoinitiator remains in its excited state, the lifetime of which is often short, the radical generation quantum yield for these compounds can be low the drawback in the usage of this method is the yellow coloring and stability of these PIs. A common issue that must be considered when choosing a photoinitiator is the maximum absorption wavelength (λ_{max}), the molar extinction coefficient (ϵ) of the photoinitiator, and the dissociation efficiency of the photoinitiators, which all determine general applicability (Sobhi, 2008) [18]. The combination of the photosensitizer camphorquinone (CQ) and co-initiator ethyl 4dimethylaminobenzoate is widely used in dental resin and adhesive formulations (Musanje *et al.*, 2009) [16]. It is essential to select photoinitiators with absorption spectra that overlap with the emission spectra of the lamp. In Light Emitting Dioxide (LED) curing lights, the broad emission spectrum ranges from 380 to 515 nm with maximum emission between 460-480 nm. A large molar extinction coefficient (ϵ) indicates a high probability of absorption at a given wavelength, leading to large quantum yields of the initiating free-organic radicals. (Neumann, 2005) [17]. The absorption range corresponds to visible blue light between 400-500nm ($\lambda_{max} = 470$ nm). The co-initiator or photo sensitizer is normally a tertiary aliphatic amine reducing agent, which reacts with camphorquinone in its excited triplet state to generate free radicals. Although several amine reducing agents are capable of providing electrons for charge transfer during the initiation process, dimethylaminoethyl dimethacrylate (DMAEMA) is commonly used. The efficiency of this is dependent upon its chemical structure and functional groups and affects clinically important properties such as the rate of polymerisation, the depth of cure and the final monomer conversion. Aliphatic amines, such as ethyl dimethylaminobenzoate and dimethylaminobenzoic acid ethyl ester may show a greater efficiency due to the aliphatic functional groups that have a greater electron density. An optimum correlation between photoinitiator and co-initiator type and concentration will maximize photon absorbance efficiency which may in turn maximize depth of cure of a filled system¹⁹. The photoinitiator concentration should be limited in order to obtain an optimum photo-curing reaction with high monomer conversion since excessive un-reacted photoinitiator, products of their photolysis, and any un-reacted monomer, may cause cytotoxicity (Pagoria *et al.*, 2005) [20]. Furthermore, the concentration of camphorquinone effects the aesthetics of a restoration as exceeding a critical concentration limit of camphorquinone will lead to yellow discoloration and any un-reacted molecules may return back to the ground state (Ogunyinka *et al.*, 2007) [21] which will cause discolouration of the final polymer. Such discoloration may reduce aesthetic quality. In acidic compositions such as enamel-dentin adhesives or self-adhesive cements containing acidic monomers, another problem may occur: The acid-base

reaction of the acidic monomers with the amine-based coinitiator may detrimentally affect the formation of radicals. In order to eliminate these disadvantages, various other substances were investigated with regard to their possible use as a substitute for amine.

4. 1-Phenyl-1, 2- propanedione

The 1-Phenyl-1, 2- Propanedione (PPD) has been suggested as a way to improve the polymerization kinetics and to reduce the "yellowing effect" of the photo-initiator. The absorption peak of this molecule is mainly in the near UV-Vis region and extends slightly into the visible region. PPD is a viable alternative in the formulation of photocured resin cements because it allows the reduction or elimination of CQ, which is yellowish, without impairing the degree of conversion, especially considering the high demand for esthetic restorations. Furthermore, both LED and QTH are effective in curing the resin cements containing PPD or CQ. However, many Light Curing Units are available on the market and each one emits light in different regions of the spectrum. Its absorption spectrum extends from below 350 nm to approximately 490 nm. The Resin Based Composites (RBCs) that only contain CQ/TA system, only require the blue spectral range (420-540 nm); however, if the RBCs contain CQ plus TPO and/or PPD, then light in both the blue (420-540 nm) and violet (360-420 nm) ranges are required. Not all curing lights deliver the required colour(s) of light and using a spectrally mismatched combination of LCU and RBC is possible. QTH LCUs have a broad spectral range corresponding with the broad spectral absorption of CQ. Both of these photo-initiators (CQ and PPD) can be used without any co-initiator in light curable dental composites, but to decrease their concentrations they are used with different co-initiators. The reason is simply that too high of a photo-initiator concentration affects the color of the dental composite. Therefore, to enhance the photo-initiator efficiency at lower concentrations, different co-initiators are added.

5. Phosphine oxides

Most of the existing photoinitiator systems for cationic polymerization are based on the use of certain onium salts such as diphenyliodonium, triphenylsulfonium, and alkoxypyridinium salts. However, these salts do not absorb significantly above 300 nm unless additional chromophores are incorporated into the salt structure. This requires multi-step synthetic and purification procedures. Naphthacene (APO), 9-anthracene (APO), and 9-anthracene (BAPO) like diphenylphosphine oxide, can be especially useful in extra white shades of resin-based composites, often required in bleached teeth since they can eliminate the unwanted yellow effect of CQ. Acylphosphine oxides (APO) are photoinitiators that undergo homolytic α -cleavage at the carbonyl-phosphorus bond to generate two free organic radicals⁴. The absorption characteristics of APO typically show enhanced absorption in the near UV/visible range. The absorption maxima is around 350-380 nm and tails around the 420 nm region (Hristova, 2005). Both photoinitiators (MAPO and BAPO) undergo fast photolysis leading to the formation of free radicals: benzoyl, phosphinyl and phosphinyl diradical⁵. These radicals show very good reactivity and the capability to initiate the polymerisation of such monomers as styrene and acrylates. However, BAPO photoinitiators are superior to MAPO and are extremely effective as they can generate four radicals from the α -cleavage of the triplet excited state. Lucirin TPO seems to be an interesting molecule despite its shorter wavelength absorption as it may provide the potential

to be a more aesthetic and a more efficient photoinitiator due to less absorption in the visible region and its much higher molar extinction coefficient, respectively. Lucirin TPO (2,4,6-trimethylbenzoyldiphenylphosphine oxide), which absorbs light in the transition area between the visible and the UVA range (max = 385 nm) and forms radicals by bond fission Ilie and Hickel (2008) demonstrated the potential for Lucirin TPO to replace camphorquinone in adhesives with regards to degree of conversion and hardness. Other investigators have also reported the possibility of improved conversion with Lucirin TPO due to the much higher molar absorptivity (Neumann *et al.*, 2005) [17]. Additionally, using camphorquinone or other photoinitiators synergistically, which have higher wavelength absorption, may aid curing at greater depths. Nevertheless, RBCs containing such initiators are limited to relatively thin specimens, which may not be a problem in flowable composites and adhesive layers of restorations.

6. Thioxanthone Derivatives

Thioxanthone (TX) and their derivatives are bimolecular Type II photoinitiators for free radical polymerization. Photoinitiation by these compounds is based on the reaction of their triplet excited states with a hydrogen donor thereby producing an initiating radical. On the other hand, they suffer from diffusion controlled limitation of reactivity and from deactivation by back electron transfer. 2-Mercaptothioxanthone (TX-SH) possesses an absorption characteristic similar to the parent thioxanthone with a maximum at 383 nm ($\epsilon = 3857 \text{ L mol}^{-1} \text{ cm}^{-1}$) [6]. This high molar absorptivity makes TX-SH attractive as a photoinitiator because of its efficient light absorption. TX-SH can be used as a photoinitiator for the polymerization of vinyl monomers in the presence and absence of air. This odorless new photoinitiator is very attractive, since it does not require an additional hydrogen donor and initiates the polymerization of both acrylate and styrene monomers in the presence and absence of air. In addition, TX-SH possesses excellent optical absorption properties in the near UV spectral region, ensuring efficient light absorption from most UV-curing tools [7]. As the other thioxanthone derivatives, thioxanthone thio-acetic acid (TX-S-CH₂-COOH) has an excellent optical absorption in the near UV ($\epsilon_{290} = 20490 \text{ mol}^{-1} \text{ L cm}^{-1}$ and $\epsilon_{384} = 3900 \text{ mol}^{-1} \text{ L cm}^{-1}$).

7. Acylgermane Derivatives

Dibenzoyl germanium derivatives are synthesized starting from various dithioacetal protected benzaldehydes by a coupling reaction with different dialkyl dichlorogermans and subsequent oxidative cleavage of the protecting group. They show a significantly stronger blue light absorption than CQ. They are used as amine free visible light photoinitiators and undergo photodecomposition under formation of radicals. Recently, organic ketones containing germanium were introduced as a new class of cleavable photoinitiators for free radical polymerization under visible light irradiation. In a process analogous to acylphosphine oxides, these photoinitiators (upon irradiation) undergo R-cleavage to produce free radicals capable of initiating polymerization of methacrylates.

BTG (in combination with suitable onium salts such as iodonium and pyridinium salts) is an efficient photoinitiator for cationic polymerization. The proposed initiation mechanism involves the photogeneration of germyl and benzoyl radicals in the first step. Subsequent oxidation of germyl radicals by onium salts yields germanium ions capable of initiating the polymerization of monomers. The efficiency

of the latter step is controlled by the redox potential of the onium salt. Acylgermane based photoinitiators can successfully be used in free radical promoted cationic polymerization of appropriate monomers. These free radical photoinitiators exhibit long wavelength characteristics due to the interaction of the lone pair of the carbonyl oxygen with the free d-orbitals of the germanium. Typical acylgermane photoinitiator, benzoyltrimethylgermane (BTG) in conjunction with an iodonium salt was shown to be active in initiating cationic polymerization of various monomers at wavelengths up to 450 nm. They are storage stable and show a significantly improved bleaching behaviour over CQ.

Benzoyltrimethylgermane (Ge-1) or dibenzoyldiethylgermane (Ge-2) represent very efficient visible light photoinitiators for methacrylate resins. In contrast to Lucirin TPO (max = 385 nm) or Irgacure 819 (max = 379 nm), Ge-1 (max = 411 nm) and Ge-2 (max = 418 nm) show a pronounced red shift in their absorption, which means that they absorb light more strongly within the visible region [8]. Moreover, compared to CQ, Ge-1 and Ge-2 demonstrate much more intensive absorption in the visible region [9]. The quantum efficiency of the light-induced cleavage for Ge-2 was determined to be 0.85, while that for Irgacure 819 was determined to be 0.59 [10]. The quantum efficiency for CQ-amine photoinitiators is below 0.10 and thus significantly lower. An analysis of dental composites containing Ge-1 or Ge-2 as photoinitiators also showed that they offer considerable advantages compared to CQ amine-based materials. Apart from demonstrating quicker curing and excellent bleaching behaviour, these materials require a much lower concentration of the photoinitiator to achieve comparable mechanical properties [11]. Similar to CQ amine-based composite resins, Ge-1 or Ge-2-based materials also show high storage stability. This also proved that when dibenzoyldiethylgermane Ge-2 is used as a photoinitiator, the benzoyl (B·) and germyl (G·) radicals produced by photolytic fission are the radicals that initiate the polymerization reaction. Based on the results of these mechanistic investigations and the evaluation of different synthesis methods and structural variations of germanium compounds, bis-(4-methoxybenzoyl) diethylgermane was selected as the optimum photoinitiator and protected by a patent under the name of Ivocerin. The novel germanium photoinitiator Ivocerin is characterized by intensive absorption of light in the visible region and high photoreactivity. Furthermore, it imparts an excellent bleaching behaviour to composite resins. The radicals required to initiate the polymerization reaction are created by light-induced cleavage of Ivocerin. Additional co-initiators or accelerators are not required. The quantum efficiency of radical formation in conjunction with Ivocerin is many times higher than that in conjunction with camphorquinone.

8. Hexaarylbiimidazole Derivatives

Hexaarylbiimidazoles (HABIs), a class of photoinitiators first synthesized by Hayashi and Maeda visible light-active photoinitiators specifically for thiol-ene systems. Upon irradiation, HABIs undergo homolytic cleavage to yield two lophyl radicals that are unreactive with oxygen and show slow recombination rates [12], attributable to steric hindrance and electron delocalization [13]. Indeed, HABI photoinitiators show no initiation activity in (meth) acrylate formulations without the presence of a hydrogen-donating coinitiator. Thiols are commonly used as coinitiators in conjunction with HABIs, where hydrogen abstraction by the HABI-derived lophyl radicals yields initiating thiyl radicals, suggesting a particular suitability for HABI photoinitiators in thiol-ene formulations [14]. Unfortunately, commercial HABIs often exhibit poor

absorption in the visible spectrum, sometimes requiring a photosensitizer, and low solubility in common resins and organic solvents [15]. Although thiol-enes show promise as continuous phases for composite dental restorative materials, they show poor reactivity with the conventional camphorquinone/tertiary amine photoinitiation system. Conversely, despite their relatively low visible light absorptivity, HABI photoinitiators afford rapid thiol-ene photopolymerization rates. Moreover, minor structural modifications suggest pathways for improved HABI solubility and visible light absorption.

9. Silane Based Derivatives

High-molecular weight, soluble and formable polysilanes have found application as photoresist materials, photo-conductors and photoinitiators in radical polymerization. These applications are mainly based on the polysilanes which have strong ultraviolet absorption in the 300–350 nm region depending on the nature of the organic substituents. Upon irradiation at this band, polysilane undergo rapid photodegradation yielding both silyl radicals and silylenes. It has been reported by West *et al.* that polysilanes are effective photoinitiators for the free radical polymerization and it was assumed that the initiating process consists of the reaction of silyl-type radicals with vinyl monomers. Recently, it was shown that in conjunction with pyridinium or iodonium salts, polysilanes can be used as photoinitiators for the cationic polymerization of cyclic ethers such as cyclohexene oxide and vinyl ethers, such as *n*-butyl vinyl ether. Polysilanes with appropriate absorption characteristics can be used successfully as a radical source in conjunction with the specially designed allylic salts to initiate cationic polymerizations via addition fragmentation mechanism.

Emission absorption matching of the LCU light output and photoinitiator light absorption is critical to adequate polymerization. The success of this technology hinges on matching the spectral emission of the LCU with the requirements of the photoinitiator system to convert the monomers into a polymer network.

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