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BAPO as an alternative photoinitiator for the radical polymerization of dental resins

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ABSTRACT

Objectives. This study evaluated the performance of phenylbis (2,4,6-trimethylbenzoyl)-phosphine oxide (BAPO) as an alternative photoinitiator in the polymerization kinetics (PK), flexural strength (σ) and elastic modulus (E) of a model dental resin.

Methods. A monomer mixture based on Bis-GMA and TEGDMA was used as model dental resin. Initially a screening was performed to evaluate BAPO concentrations (0.125, 0.25, 0.50, 1, 2, and 4 mol%). Photoinitiator systems were formed with the combination of camphorquinone (CQ), ethyl-dimethylamino benzoate (EDAB), diphenyliodonium hexafluorophosphate (DPIHFP), and BAPO. Groups with unitary photoinitiator systems (BAPO and CQ), binary (BAPO + EDAB, BAPO + DPIHFP and CQ + EDAB), ternary (BAPO + CQ + EDAB, BAPO + CQ + DPIHFP, BAPO + EDAB + DPIHFP and CQ + EDAB + DPIHFP) and quaternary (BAPO + CQ + EDAB + DPIHFP) were formulated for evaluation. Real-time Fourier transform infrared spectroscopy was used to investigate the PK and test mini-bending to evaluate σ and E.

Results. When only CQ was used, a slow polymerization reaction was observed and a lower monomer conversion. When only BAPO was used as photoinitiator an increase in the polymerization rate was observed and conversion was higher than CQ + EDAB. The ternary system (BAPO + EDAB + DPIHFP) showed the highest polymerization and conversion rate, in short photo-activation time.

Significance. BAPO it is a potential photoinitiator for the photopolymerization of dental materials.

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1. Introduction

Since an efficient radical polymerization initiator is an extremely valuable component of light-curing dental adhesives and resin composites, studies have been conducted to identify and develop the most effective photoinitiator systems. The degree of conversion of methacrylate-based materials is a modulator of the physical, biological and mechanical properties of the polymer [1–3]. The degree of conversion is influenced by multiple factors, such as the methacrylate monomer type, the photoinitiator light absorption range on the region of the emitted spectrum, light intensity used for irradiation, and the kind and concentration of the initiation system [4,5].

Photoinitiation systems used for radical polymerization of methacrylate-based materials are classified based on the mechanism of formation of free radicals after light absorption: Type I systems generate radicals by fragmentation of the photoinitiator molecule and Type II photoinitiators in their excited state need to interact with a co-initiator, donor of electrons and protons, so the radicals can be generated [6].

Of the initiation systems, the most commonly used in dental resins is the type II formed by two components: the photoinitiator camphorquinone (CQ), which after being activated by visible light absorbance between 450 and 500 nm ($\lambda_{max} = 468$ nm) requires a co-initiator like an amine, which donates hydrogen to generate the radical polymerization of the resin [7], whereas the energy of a photon at 468 nm is insufficient to directly cleave an initiator to carbon-based radicals. Although this system is commonly used, it can compromise esthetic restorations because CQ has a yellowish color and amine suffers yellowing over time [7–9]. Moreover, CQ and EDAB have been identified in eluates of methacrylate-based materials showing cytotoxic effects such as increase in the amount of intracellular formation of reactive oxygen species (ROS) [10], increase in the intracellular glutathione (GSH) content [11], and breaks in the integrity of DNA in cultured cells [12].

With those characteristics, the importance of investigate the alternative initiators to be included in the formulation of new dental resin products has been verified [13–17]. An oxide bisacylphosphine, photoinitiator type I, with part of its absorption in the visible spectrum between 365 and 416 nm ($\lambda_{max} = 371$ nm), has shown advantages such as white coloration of the compound that could help the incident light penetration and at the same time increase the polymerization depth through the resin, as it has high reactivity, and because it, is unnecessary to use amine as a co-initiator in this initiation system [18,19].

Previous studies have proved that the polymerization behavior of dental monomers is beneficial when the iodonium salt is added to the CQ-based systems [14,15]. However, little information exist about the efficiency when the aforementioned components are associated with BAPO, and this question needs clarification. Therefore, the aim of this study was to evaluate the performance of the phenylbis (2,4,6-trimethylbenzoyl)-phosphine oxide (BAPO) as a radical photoinitiator, solely or associated with other initiators, as an alternative to the traditional CQ-based systems in a model dental resin through the polymerization kinetics and mechanical properties of the polymer. The hypotheses tested where that; (1) the photoinitiator BAPO is able to promote satisfactory polymerization and (2) the combination of BAPO and co-initiators may improve the polymerization efficiency of a model dental resins.

2. Materials and methods

2.1. *Reagents*

Bisphenol A glicidyl dimethacrylate (Bis-GMA), triethylene glycol dimethacrylate (TEGDMA) and camphorquinone (CQ) were supplied by Esstech Inc. (Essington, PA, USA). Ethyl 4-dimethylaminobenzoate (EDAB), phenylbis (2,4,6-trimethylbenzoyl)-phosphine oxide (BAPO) and diphenyliodonium hexafluorophosphate (DPIHFP) were purchased from Aldrich Chemical Co (Milwaukee, WI, USA). All reagents were used as received without further purification. Characteristics of the initiators used in this study are shown in Table 1.

2.2. *Formulations*

A model dental resin was formulated through intensive mixing of 50 wt% Bis-GMA and 50 wt% TEGDMA. The formulation was carried out in two steps:

- Evaluation of different concentrations of photoinitiator BAPO: The alternative photoinitiator was tested at various molar concentrations: 0.125, 0.25, 0.50, 1, 2, and 4 mol%, according to the monomer moles. After this initial screening, the photoinitiator concentration that showed the best performance was used in the experimental groups.
- Evaluation of different initiation systems composition: Ten combinations of photoinitiator and/or co-initiator were investigated and are showed in Table 2.

2.3. *Kinetics of polymerization by RT-FTIR spectroscopy*

The degree of conversion from the experimental materials was evaluated using real-time Fourier transform infrared spectroscopy with a spectrometer (Model IR-Prestige 21, Shimadzu Corporation, Japan) equipped with an attenuated total reflectance device, composed of a horizontal ZnSe crystal, with a 45° mirror angle (PIKE Technologies, Madison, WI, USA). The halogen light-curing unit (XL 3000, 3M ESPE, St. Paul, MN, USA) was fixed with a support coupled to the spectrometer to keep a distance of 5 mm between the fiber tip and the sample during light activation. The irradiation values (450 $\mathrm{mW/cm^2}$) were confirmed with a digital power meter (Ophir Optronics, Danvers, MA, USA).

The IR Solution software (Shimadzu, Columbia, MD, USA) was used in the monitoring scan mode, using the Happ-Genzel appodization, at a range of 1750 and 1550 $\mathrm{cm^{-1}}$, resolution of 8 $\mathrm{cm^{-1}}$ and mirror speed of 2.8 mm/s. Each sample was directly dispensed (3 μL) on the ZnSe crystal and light activation was performed for 60 s. With this setup, one scan every 1 s during photo-activation was acquired. Analysis was performed at a