

# Alternative Cointiators Applicable to Photocurable Resin Composites

Bruna Fortes Bittencourt<sup>1</sup>, John Alexis Dominguez<sup>1</sup>, Paulo Vitor Farago<sup>2</sup>, Luis Antonio Pinheiro<sup>3</sup>, Osnara Maria Mongruel Gomes<sup>1</sup>

<sup>1</sup>Department of Dentistry, State Ponta Grossa University, Carlos Cavalcanti, 4748 – Uvaranas, 84030-900, Ponta Grossa, Paraná, Brazil. <sup>2</sup>Department of Pharmaceutical Sciences, State Ponta Grossa University, Carlos Cavalcanti, 4748 – Uvaranas, 84030-900, Ponta Grossa, Paraná, Brazil, Paraná, Brazil. <sup>3</sup>Department of Materials Engineering, State Ponta Grossa University, Carlos Cavalcanti, 4748 – Uvaranas, 84030-900, Ponta Grossa, Paraná, Brazil, Paraná, Brazil.

## Abstract

This review aimed to examine the evolution of the composite resins's photoinitiator system, with emphasis on those developed in recent years. This review covered literature from 1990 to 2013 and only papers with the key words of interest were included: "cointiators", "amines", "composite resins", "photopolymerization". The search used full-text papers from PubMed and Science Direct databasis. It was included only English papers, and meeting abstracts and short communications were excluded. Hand search of the references completed the review. A total of 29 articles were studied. Many cointiators are being researched as an alternative to traditional tertiary amines, particularly in order to improve the physical and mechanical properties of the final polymer and its biocompatibility with oral tissues. Polymerizable amines, natural compounds, and cointiators with low toxicity and antiseptic properties were studied, and the results found they would be promising substitutes. These materials must present appropriate concentration and reactivity to obtain adequate physical and mechanical properties and high biocompatibility. However, further in vivo studies are required to verify the performance of these alternative cointiators in the composite materials, mainly when in contact with oral tissues and the stomatognathic system.

*Key words: Resin composites, Photopolymerization, Cointiators.*

## Introduction

The composite resins available on the market today are mostly light-cured resins. So, photoinitiator molecules are included in these materials which have the ability to absorb light, and as result, generate free radicals which initiate the polymerization of these resin materials [1].

The light curing systems most commonly employed in the composites are the camphorquinone/amine system. The photoinitiator is camphorquinone, which requires a cointiator to perform the polymerization process. Tertiary amines (aliphatic or aromatic) do not absorb light, but interact with the activated camphorquinone to produce reactive species [2,3]. However, this photoinitiator system has some disadvantages, such as the tendency to promote yellowing to resin materials [4,5] low compatibility with oral tissues [6-8] and even mutagenic characteristics [9].

It is well understood that factors such as type of photoinitiator [10-12], photoinitiator/cointiator ratio [13,14], type and concentration of cointiator [10,15] may influence the properties of the resin materials. These properties range from polymerization rate, degree of conversion, the shrinkage stress, the (micro)hardness, aesthetic impairment and biocompatibility of the materials.

For certain resinous systems, one way to reduce toxicity, enhance color stability without compromising the physical and mechanical properties of polymers with camphorquinone/amine is to explore new substitutes already used on the market [16-18]. These molecules must show high reactivity and high degree of monomer conversion, since no reactive monomers may diffuse out of the polymer matrix to the oral cavity [16]. Based on the aforementioned facts, the objective of this review was to discuss the evolution of the cointiators of

composite resins, focusing on their physico-chemical, mechanical and biological characteristics.

## Review

This review covered literature from 1990 to 2013 and only papers with the key words of interest were included: "cointiators", "amines", "composite resins", "photopolymerization". The search used full-text papers from PubMed and Science Direct databasis. It was included only English papers, and meeting abstracts and short communications were excluded. Hand search of the references completed the review.

The first composites materials commercially available were based on Bisphenolglycidylmetacrilate (Bis-GMA) with chemical polymerization, or selfcured resins. This reaction was produced by mixing two pastes, one containing the initiator and the other an activator product, benzoyl peroxide and Dimethyl Paratoluidine (DMT), a tertiary amine, respectively. However, the chemically cured resins had some disadvantages: it is impossible to control working time, color instability [19], high viscosity [20]. It did not take so far for the photoactivated resins being widely used by dentists. The first commercially available light-cured resin composite was NuvaFil (Dentsply). Among its advantages over chemical resins, some are listed: a single paste, which did not require mixing and full control of working time by the operator, with fast curing and start at the operator's command [1,21], as well as easy sculpture [21]. Briefly, the reaction of curing includes three stages: 1) initiation: after the incidence of blue light (wavelength 468 nm) on the composite resin, Camphorquinone (CQ) enters the exciplex state, making it able to react with the cointiator (one electron transfer to the amine). From this reaction free radicals, which show reactivity to break the unsaturated carbon bonds of the

Corresponding author: John Alexis Dominguez, Alameda Nabuco de Araujo 422 - Ponta Grossa, Paraná, Brazil; Tel: 55-42-32245164; Fax: 55-42-32241166; e-mail: johnalexis.dominguez@gmail.com

monomer, through hydrogen abstraction, called the propagation phase (2) are formed. These monomers are connected to other monomers that have been broken, in a chain reaction, forming the polymer. Finally, the termination (3) occurs when the active two chain ends react together and form an inactive macromolecule, ending the chain growth [1,22,23].

Tertiary amines are commonly used as coinitiators because they facilitate the formation of alpha-amino alkyl radicals and due to its high reactivity at lower concentrations [24]. The polymerization reaction of the composites depends not only on the reactivity of the amines as coinitiator, but also the molar absorption coefficient of the photoinitiator, which is the ability of this molecule (usually CQ) to absorb photons of the light unit and generate free radicals in its excitatory state [1]. The primary amines used in the photoactivated composites are basically Dimethylaminoethylmetacrylate (DMAEMA) and Ethyl-4-dimethylaminobenzoate (EDMAB).

Some disadvantages of aromatic tertiary amines may be verified, as previously mentioned. Historically, Brauer et al. analyzed 15 different types of aromatic tertiary amines on chemically activated resins, and found that all these amines showed color change in different degrees [24]. Schneider et al. found that the concentration of the photoinitiator/coinitiator system is responsible for a greater degree of yellowing of the composite [5,10]. The biocompatibility of aromatic tertiary amines is the most worrying feature of these components, subject of many studies. Vasquez et al. studied the biocompatibility (by intravenous injection in rats) of alternative amines compared to DMT used for the polymerization of bone cements: 4-Dimethylaminobenzyl alcohol (DMOH) and 4-dimethyl-aminobenzylmethacrylate (DMMO) [7]. Alternative coinitiators were shown three times less toxic compared to DMT, and favorable mechanical characteristics to bond cements. Liso et al. also found that in terms of acute toxicity and cytotoxicity, both DMOH and DMMO amines are less aggressive than DMT [6], and some antiseptic characteristics, which was very interesting for orthopedics and dentistry, as these materials keep in contact with human tissues. Masuki et al. assessed the necrotic potential of camphorquinone, benzoyl peroxide, DMT and DMAEMA on human gingival fibroblasts and concluded that the 4 components of resin materials exhibited a necrotic effect [25].

Also, it was verified that Bis-GMA based-materials had no complete conversion of the carbon double bonds and polymerization shrinkage, the latter resulting in stress development on tooth structure [26,27]. And these characteristics were directly related to several factors, among them the photoinitiator/coinitiator system, which may be:

1. With respect to the photoinitiator type: Schneider et al. evaluated CQ [5], phenylpropanedione (PPD) and the combination of CQ/PPD on degree of conversion (DC) and the maximum degree of polymerization (MDP), verifying that the PPD and the combination of CQ/PPD decreased this latter property, which in turn is influenced by the power intensity absorption, and the degree of conversion. Schneider et al. evaluated the same groups of the previous study on characteristics such as the shrinkage stress, DC, MDP and

cross-linking density [12]. They found that the combination of CQ/PPD may be promising, since the developing stress was decreased, without compromising the final properties of the polymer. Leprince et al. compared Lucirin-TPO (TPO) and CQ on the DC and depth of cure of composites [15], and observed that the DC is higher for samples made of TPO, while the depth of cure is higher for samples with CQ. Costa Oliveira et al. also evaluated the polymerization stress in experimental resins formulated with CQ, PPD or combination of both, as well as two commercial resins (Filtek Z250 and Filtek Silorane) finding that just silorane-based resin decreased the effects of stress polymerization, thus decreasing gap formation [11]. Cunha Brandt et al. assessed three types of combinations of photoinitiators (CQ, PPD, CQ/PPD) on various mechanical properties including compressive strength, diametral strength, elastic modulus and DC [28]. It was found that the photoinitiators behaved similarly, concerning the properties analyzed.

2. Photoinitiator/coinitiator ratio: Schneider et al. evaluated 4 experimental resins with different CQ/EDMAB ratios (2:1, 1:1, 1:1.15, 1:2) on DC and MDP [12]. The higher the EDMAB ratio, the greater is the the final properties of the polymer. Musanje et al. evaluated 25 experimental conditions to see which CQ/EDMAB ratio was ideal to have maximum DC and minimal stress development [13]. They concluded that there are several combinations of CQ/EDMAB which generate an appropriate degree of polymerization of composite resins, but to have a low degree of shrinkage stress, QC/EDMAB should be decreased, which, in turn, compromises properties such as DC and surface hardness of the polymer.

3. The type and concentration of the coinitiator also has great influence on the final properties of the polymer. Among the innovations, new coinitiators, substitutes for conventional DMT amines, DMAEMA and EDMAB, were developed:

- A. 'Natural' Coinitiators (Benzodioxole BDO, sesamin and its derivatives): Liu et al. evaluated BDO and piperonyl alcohol benzodioxole (PA) [29]. The properties evaluated were: DC, modulus and glass transition temperature, as well as sorption and solubility, which showed excellent results. Thus, the authors concluded that BDO and PA would be viable alternatives to conventional amines. Shi and Nie evaluated BDO and compared it to EDMAB in combination with CQ at different concentrations (0, 0.5, 1.0 and 2.0wt% of EDMAB and BDO, and 0, 0.2, 0.5, 0.8, and 1.0wt% of CQ) and a combination of both [16]. It was evaluated the same properties as Liu et al. and found a similar behavior to the resins formulated with EDMAB or BDO [29]. For the authors, the BDO is a promising alternative coinitiator to conventional amines. Shi and Nie observed the potential of 3,4-methoxymethacrylate methylenedioxybenzene (MDBMM) as coinitiator, showing favorable results in terms of DC and reactivity, comparable to control (DMAEMA) [30]. This coinitiator presents benzodioxole and methacrylate radicals, acting also like a photopolymerizable amine. Wang et al. synthesized and characterized sesamin, and compared some of its mechanical properties and cytotoxicity with EDMAB [18]. The results showed that although DC of the resin with sesamin were slightly lower than EDMAB samples, the tendency to yellowing was lower and the values of

sorption and solubility were similar, with satisfactory biocompatibility. Shi synthesized and characterized three derivatives of BDO (MDBMM; 3,4-methylenedioxybenzene methoxyacetate -MDBMA; sesamolmethacrylate -SMA), measuring their reactivity, mechanical properties and cytotoxicity of Bis-GMA and TEGDMA polymers [31]. The EDMAB and DMAEMA were used for comparison purposes. The results showed that the derivatives of BDO demonstrated high reactivity to generate free radicals and mechanical properties comparable to controls, and also high biocompatibility.

**B. Polymerizable Amines:** Nie and Bowman evaluated NDMH (N'-dimethyl,-N'-di[methacryloxyethyl]-1,6-hexanediamine) with two different functions: as a possible substitute for the conventional coinitiator and as a substitute for the diluent monomer TEGDMA [32]. It was performed the synthesis and characterization of NDMH and tests of DC, glass transition temperature, elastic modulus were made. Sorption and solubility were also measured, and a conventional curing system (Bis-GMA/TEGDMA/CQ/EDAB) was examined as control. The concentration ranged from 0.05 to 4wt% of NDMH in the experimental groups. NDMH has been found to be a possible substitute to conventional amine and diluent monomer, as similar physical properties to control were found. Also, Wu and Nie evaluated the two most common coinitiators (EDMAB and DMAEMA) and an alternative one: DMPDA (N,N-dimethyl-N 'N'-di[2-(methylacryloyl)ethoxycarbonyl] propylidiamine) in concentrations ranging from 0 to 0.5wt% [33]. After performing the synthesis and characterization of the alternative coinitiator, the following properties were evaluated: DC, modulus and glass transition temperature, sorption and solubility. The results showed that resin blends made of DMPDA in the concentration of 0.5wt% was the one with the lowest DC and the lower final value of conversion of carbon double bonds, lower than the commercially available amines. Wu and Nie also synthesized and characterized the 3-diethylamino-propionate methacrylate (EGDPM), comparing it with EDMAB and DMAEMA coinitiators [17]. The mechanical properties, sorption and solubility of the resin samples were evaluated. The tests showed that despite groups had similar values of sorption and solubility, DC and the rate of polymerization of the resin made of EGDPM were lower than the controls EDMAB and DMAEMA, even at concentrations of 0.25 wt%.

**C.** Among the coinitiators studied, a tertiary amine, developed by Vazquez et al. [7] DMOH, which is used in bone cements, was evaluated by Schroeder et al. [14] with the proposal to be an alternative coinitiator to resin-based Bis-GMA and TEGDMA materials with CQ. DMAEMA was used as control. The authors found high DC values, at lower concentrations (less than 0.25%). In this study, the effectiveness of CQ/DMOH, in terms of radical formation and final monomer conversion was higher than that of CQ/DMAEMA.

**D. Barbituric Acid Derivatives:** Münchow et al. [34] on the premise that the EDMAB would be unstable in acidic environments, evaluated TBA (1,3-Diethyl-2-thiobarbituric acid) as possible coinitiator of an experimental adhesive. It was evaluated the Kinetics of Polymerization (KP), DC and

the rate of polymerization. Six groups were made: Four of TBA containing different concentrations (0.1, 0.5, 1, and 2 mol%), a free coinitiator sample and 1 mol% of EDMAB (control). The results showed that DC increased as the concentration of TBA was higher, and the group with 2 mol% of TBA showed the best results of DC and reactivity, being considered an efficient alternative coinitiator. Although this experiment was conducted with an experimental adhesive, the authors report it may be used with composite resins.

## Discussion

The effectiveness of CQ/tertiary amine system clinically affects important properties of the composite such as polymerization rate, depth of cure and the final DC [31]. This efficiency is related to the concentration and the structure of the amine [17,35]. In almost all studies analyzed, the rate of polymerization and DC increased as the concentrations of coinitiators increased. However, besides the concentration, the reactivity of the molecule also has great influence on the properties of the final polymer. This reactivity is related to the chemical structure of tertiary amines [4]. The reactivity reflects on the formation of aminoalkyl radicals, which in turn modulate the polymerization kinetics, especially in the early stages of this reaction. Thus, the physical and mechanical properties of the final polymer will be directly linked to the type and concentration of the amine used in photoinitiator system [31,35,36]. Is due to these characteristics the fact that studies analyzing different concentrations of the same coinitiator found better mechanical properties when there is an increased concentration of them [10,33,34], and studies that evaluated different coinitiators found that the one which presented the best physical-mechanical properties of the final polymer also showed higher reactivity [14,16,31,35].

Generally, tertiary amines are more reactive. Among the tertiary amines, aromatic may generate more radicals than aliphatic amines [37]. This fact was observed in other study, which DMPDA - an aliphatic amine, showed the best results in DC, modulus and glass transition temperature, sorption and solubility, followed by DMAEMA (aliphatic, but lower reactive than DMPDA). EDMAB (aromatic amine) showed the lower results [33]. Also, the DMAEMA radical-containing methacrylate, which acts as a photopolymerizable amine and may increases DC values and consequently the physical-mechanical properties of the polymer, even when used in small quantities [35].

A review about the substances released by resin restorative materials clearly demonstrated that molecules incorporated to resin composites are able to cause toxic and genotoxic effects in relevant concentrations in the oral cavity [38]. From these studies, it was found that the main concern with amines is actually their biocompatibility. In some studies, it was suspected that they would be mutagenic [9]. Conventional amines, with low molecular weight, do not polymerize and spread to adjacent tissues and oral environment, and due to its basic character, become damaging to tissue [4]. Some alternatives have been proposed to reduce this diffusion to as minimum as possible. One of them was to incorporate a polymerizable amine, by adding a methacrylate radical [17,32,33]. This copolymerization with the monomer through the methacrylate group increases the biocompatibility of the

final polymer, as increased DC values are obtained, which leads to a reduced release of the material components in the oral cavity [17]. Another alternative was the use of natural coinitiators for resin composites, as the benzodioxole derivatives and sesamin. In the analyzed studies, besides these natural coinitiators present high reactivity at low concentrations, appropriate physical and mechanical properties were found [16,29-31]. Also, Wang et al. showed in an *in vitro* study, low cytotoxicity of the natural derivatives [18].

The inclusion of coinitiators used in orthopedic bone cements was also verified for composites. Schroeder et al. proved that DMOH was a promising alternative, due to its higher reactivity compared to DMAEMA, even at low concentrations [14]. This coinitiator also demonstrates highly biocompatible and, in other studies that evaluated DMOH in bone cements, its antiseptic and bactericidal properties were clearly positive [6,7,39].

Based on what was raised by this review, the alternative is to explore possible replacements for amines commonly used in the composites, so that new coinitiators may be used in the formulations of these materials. Their great evolutions have spin around the development of materials with high mechanical properties, and few industries are concerned to develop resins with high biological properties [38]. The coinitiators must not only exhibit high reactivity at low concentrations to produce a final polymer with high physical and mechanical properties as well as high biocompatibility. Likewise these molecules must be capable to form highly radicals to break the unsaturated carbon bonds of the monomers and reaching high conversion, producing a minimum amount of residual monomers, since they also have potential cytotoxic effects to oral tissues.

## Conclusions

It may be concluded that many alternative coinitiators have been analyzed and most of these substances show promising results. These coinitiators should present appropriate concentration and reactivity to obtain adequate physical and mechanical properties and high biocompatibility. However, further *in vivo* studies are needed to verify the performance of these alternative coinitiators in the composites, especially in order to verify their interaction with oral tissues and in function with stomatognathic system.

## References

1. Stansbury JW. Curing dental resins and composites by photopolymerization. *Journal of Esthetic Dentistry*. 2000; **12**: 300-308.
2. Jakubiak J, Allonas X, Fouassier JP, Sionkowska A, Andrzejewska E, Linden LA, et al. Camphorquinone-amines photoinitiating systems for the initiation of free radical polymerization. *Polymer*. 2003; **44**: 5219-5226.
3. Jakubiak J, Wrzyszczyński A, Linden LA, Rabek JF. The role of amines in the Camphorquinone photoinitiated polymerization of multifunctional monomer. *Journal of Macromolecular Science*. 2007; **44**: 239-242.
4. Bowen RL, Argentar H. Tertiary Aromatic Amine Accelerators with Molecular Weights Above 400. *Journal of Dental Research*. 1972; **51**: 473-482.
5. Schneider LFJ, Pfeifer CSC, Consani S, Prahl SA, Ferracane JL. Influence of photoinitiator type on the rate of polymerization, degree of conversion, hardness and yellowing of dental resin composites. *Dental Materials*. 2008; **24**: 1169-1177.
6. Liso PA, Vazquez B, Rebuella M, Hernandez ML, Rotger R, San Roman J. Analysis of the leaching and toxicity of new amine activators for the curing of acrylic bone cements and composites. *Biomaterials*. 1997; **18**: 15-20.
7. Vázquez B, Elvira C, Levenfeld B, Pascual B, Goni I, Gurruchaga M, et al. Application of tertiary amines with reduced toxicity to the curing process of acrylic bone cements. *Journal of Biomedical Materials Research*. 1997; **34**: 129-136.
8. Achilias SD, Sideridou ID. Kinetics of the benzoyl peroxide/amine initiated free-radical polymerization of dental dimethacrylate monomers: experimental studies and mathematical modeling for TEGDMA and Bis-EMA. *Macromolecules*. 2004; **37**: 4254-4265.
9. Kucybala Z, Pietrzak M, Paczkowski J. Kinetic studies of a new photoinitiator hybrid system based on Camphorquinone-N-phenylglycine derivatives for laser polymerization of dental restorative and stereolithographic (3D) formulations. *Polymer*. 1996; **37**: 4585-4591.
10. Schneider LF, Consani S, Sakaguchi RL, Ferracane JL. Alternative photoinitiator system reduces the rate of stress development without compromising the final properties of the dental composite. *Dental Materials*. 2009; **25**: 566-572.
11. Costa Oliveira KM, Consani S, Gonçalves LS, Brandt WC, CCahuana-Vásquez RA. Photoelastic evaluation of the effect of composite formulation on polymerization shrinkage stress. *Brazilian Oral Research*. 2012; **26**: 202-208.
12. Schneider LF, Cavalcante LM, Consani S, Ferracane JL. Effect of co-initiator ratio on the polymer properties of experimental resin composites formulated with camphorquinone and phenylpropanedione. *Dental Materials*. 2009; **25**: 369-375.
13. Musanje L, Ferracane JL, Sakaguchi RL. Determination of the optimal photoinitiator concentration in dental composites based on essential material properties. *Dental Materials*. 2009; **25**: 994-1000.
14. Schroeder WF, Cook WD, Vallo CI. Photopolymerization of N,N-dimethylaminobenzyl alcohol as amine co-initiator for light-cured dental resins. *Dental Materials*. 2008; **24**: 686-693.
15. LePrince JG, Hadis M, Shortall AC, Ferracane JL, Devaux J, Leloup G, et al. Photoinitiator type and applicability of exposure reciprocity law in filled and unfilled photoactive resins. *Dental Materials*. 2011; **27**: 157-164.
16. Shi S, Nie J. A Natural Component as Coinitiator for Unfilled Dental Resin Composites. *Journal of Biomedical Materials Research Part B: Applied Biomaterials*. 2007; **82**: 44-50.
17. Wu G, Nie J. Synthesis and evaluation of ethylene glycol 3-diethylamino-propionate methacrylate as a polymerizable amine coinitiator for dental application. *Dental Materials*. 2007; **23**: 623-629.
18. Wang K, Yang D, Xiao M, Chen X, Lu F, Nie J. Sesamin as a co-initiator for unfilled dental restorations. *Acta Biomaterialia*. 2009; **5**: 2508-2517.
19. Bowen RL, Rodriguez MS. Tensile strength and modulus of elasticity of tooth structure and several restorative materials. *Journal of the American Dental Association*. 1962; **64**: 378-387.
20. Rueggeberg FA. From vulcanite to vinyl, a history of resins in restorative dentistry. *Journal of Prosthetic Dentistry*. 2002; **87**: 364-379.
21. Sheykholeslan Z, Houpt MI. Use of the ultraviolet light polymerized adhesive (Nuva-Seal and Nuva-Fil) in clinical Dentistry. *Quintessence International*. 1979; **10**: 17-21.
22. Anusavice KJ. Phillips' Science of Dental Materials. (13th edn.) St Louis: Elsevier Health Sciences; 2003. pp. 832.
23. Reis A, Loguercio AD. Materiais Dentários Diretos: dos fundamentos à aplicação clínica. (1st edn.) São Paulo: Santos, 2009. pp. 423.

24. Brauer GM, Dulik DM, Antonucci JM, Termini DJ, Argentar H. New Amine Accelerators for Composite Restorative Resins. *Journal of Dental Research*. 1979; **58**: 1994-2000.
25. Masuki K, Nomura Y, Bhawal UK, Sawajiri M, Hirata I, Nahara Y, et al. Apoptotic and Necrotic Influence of Dental Resin Polymerization Initiators in Human Gingival Fibroblast Cultures. *Dental Materials Journal*. 2007; **26**: 861-869.
26. Lovelth LG, Newman SM, Bowman CN. Behavior of Dimethacrylate Dental Resins The Effects of Light Intensity, Temperature, and Comonomer Composition on the Polymerization. *Journal of Dental Research*. 1999; **78**: 1469-1476.
27. Cramer NB, Stansbury JW, Bowman CN. Recent Advances and Developments in Composite Dental Restorative Materials. *Journal of Dental Research*. 2011; **90**: 402-416.
28. Brandt WC, Silva CG, Frollini E, Souza-Junior EJ, Sinhoreti MA. Dynamic mechanical thermal analysis of composite resins with CQ and PPD as photo-initiators photoactivated by QTH and LED units. *Journal of the Mechanical Behavior of Biomedical Materials*. 2013; **24**: 21-29.
29. Liu S, Shi S, Hou G, Nie J. Benzodioxole derivative as coinitiator for dental resin. *Acta Odontologica Scandinavica*. 2007; **65**: 313-318.
30. Shi S, Nie J. Investigation of 3,4-Methylenedioxybenzene Methoxyl Methacrylate as Coinitiator and Comonomer for Dental Application. *Journal of Biomedical Materials Research Part B: Applied Biomaterials*. 2007; **82B**: 487-493.
31. Shi S, Xiao P, Wang K, Gong Y, Nie J. Influence of chemical structures of benzodioxole-based coinitiators on the properties of the unfilled dental resin. *Acta Biomaterialia*. 2010; **6**: 3067-3071.
32. Nie J, Bowman CN. Synthesis and photopolymerization of N,N'-dimethyl,-N,N'-di(methacryloxy ethyl)-1,6-hexanediamine as a polymerizable amine coinitiator for dental restorations. *Biomaterials*. 2002; **23**: 1221-1226.
33. Wu G, Nie J. Synthesis and evaluation of N,N-dimethyl-N',N'-di[2-(methacryloyl)-ethoxycarbonyl]propylidiamine as a coinitiator. *Journal of Photochemistry and Photobiology A: Chemistry*. 2006; **183**: 154-158.
34. Munchow EA, Valente LL, Peralta SL, Fernandez MR, Lima GS, Petzhold CL, et al. 1,3-Diethyl-2-thiobarbituric acid as an alternative coinitiator for acidic photopolymerizable dental materials. *Journal of Biomedical Materials Research Part B: Applied Biomaterials*. 2013; **10**: 1217-1221.
35. Yoshida K, Greener EH. Effects of two amine reducing agents on the degree of conversion and physical properties of an unfilled light-cured resin. *Dental Materials*. 1993; **9**: 246-251.
36. Yoshida K, Greener EH. Effect of photoinitiator on degree of conversion of unfilled light-cured resin. *Journal of Dentistry*. 1994; **22**: 296-299.
37. Cook WD. Photopolymerization kinetics of dimethacrylates using the camphorquinone/amine initiator system. *Polymer*. 1992; **33**: 600-609.
38. Bakopoulou A, Papadopoulos T, Garefis P. Molecular Toxicology of Substances Released from Resin-Based Dental Restorative Materials. *International Journal of Molecular Sciences*. 2009; **10**: 3861-3899.
39. de la Torre B, Salvado M, González Corchón MA, Vázquez B, Collía F, De Pedro JA, et al. Biological response of new activated acrylic bone cements with antiseptic properties. Histomorphometric analysis. *Journal of Materials Science: Materials in Medicine*. 2007; **18**: 933-994.