



Living Polymerization Techniques and Their Utility in Material Synthesis

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Abstract

The polymeric materials are used in several applications. An adequate polymerization of these materials is fundamental to improve the physical and chemical properties. The aim of this study was related some findings of role of polymerization techniques on the behavior of resin-based materials.

Introduction

The polymer-based materials have been used in several applications. In contemporary dentistry these materials are frequently used and light curing is commonly required during clinical procedures. The professionals daily performed the polymerization of monomers into polymers as a simple process, but several implications are present in this reaction.

Initiator

In the late 1940s the use of acrylic resin for esthetic restorations was usual. However, with development of Bis-GMA by Bowen in the early 1960s, the resin-based materials were rapidly applied in the dental restorations [1].

The first composites resins were self-cured, paste-paste system; these materials used the benzoyl peroxide as initiator of the polymerization reaction [2]. In 1970 the light-activated composites were introduced, maximizing working time and minimizing setting time [3], and camphorquinone (CQ) has been the photoinitiator more used [2,4]. Recently, due to the greater demand for esthetic treatments the search for bleaching procedure has increased, but the restorations of bleached teeth with CQ-based dental composites is compromised in most cases, because this photoinitiator is yellowish, thus others initiators have been used, such as 2,4,6-trimethylbenzoyl-diphenylphosphine oxide and bis(2,3,6-trimethylbenzoyl)-phenylphosphineoxide [4].

Polymerization reaction

The most contemporary dental materials are light-activated and use the popular basic formulation composed by a visible light-curing photoinitiation system composition (generally CQ) and a tertiary amine co-initiator introduced to many years and, which remains in use today [4].

The polymerization reaction occurs when the initiator molecule absorbs a photon of light (for CQ approximately 470 nm wavelength) [5], an electron of this molecule is boosted to a higher level of energy, leaving it a triplet state excitation [6]. Thus, the photoinitiator collides with tertiary amine, and the free radicals amino and ketyl are formed. This amino radical can react with a carbon double bond (C=C) in the aliphatic group of the monomer chains, initiating the polymerization reaction, in which monomers that have a C=C bond broken in one or the two ends react with other monomers in the same situation forming polymer structure [4,7].

Light-curing units

The first Light-Curing Unit (LCU) emitted ultraviolet radiation through a quartz rod from a high-pressure mercury source [4]. However, this device showed some deficiencies, such as ability of the light to penetrate within material limited in depth, potential for harmful effects of the short wavelength energy being exposed to human eyes, and changes in the oral microflora [4,8,9]. In an attempt to solve some these problems was developed the LCU that emits visible radiation. The device consists of a quartz-tungsten-halogen (QTH) lamp and a bandpass filter, which allows pass only light between 400 to 550 nm of wavelengths [4]. QTH unit has been used for a long time, but bulb overheating results in light power reduction over time due to the lamp and filter degradation [10]. The laser unit was initially in dentistry to improve vital dental bleaching efficacy

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[11]. Posteriorly it was used to cure light-activated materials, obtaining adequate physical properties of restorative materials [12]. However, this device has elevated cost and only a clinician could operate the unit, besides some researchers relate that individual energy delivery for optimal performance is necessary for each brand and shade of composite [4,13].

Plasma-arc curing (PAC) source was imported from Europe due to dental auxiliary personnel was prohibited to use the laser in USA. A high light emission is created by the electrical current generates between two electrodes separated by a small distance in a high-pressure ionized gas chamber [4,14]. The first devices required filter because infrared light and ultraviolet is generated, but later these units were adapted in visible light wavelength. The light output is extremely high (~2000 mW/cm²) and materials can be photopolymerized with short time, but rapid polymerization can compromise the marginal adaptation of restorations and PAC units are expensive [1,14]. The light-emitting diode (LED) technology was introduced more recently for use in dentistry and considered a light source efficient and cost-effective. These units have peak wavelength near from maximum absorption of CQ, lower degradation, and no filter is necessary, due to emission of blue light spectrum [4,10]. The first generation LED was introduced at the end of 2000, however it had a typical design of an assemblage of multiple LED elements (5 mm lamp, individual), array from 7 to 64 were available, resulting in low luminance difficult the competition with standard QTH unit [4].

Advances in LED industry technology allowed changing multiple emitting lamps for a single chip, with similar luminance as 10-20 individual 5 mm lamp of the 1st generation. Thus, the second generation LED increased the irradiance, but a similar wavelength range persisted and inability to light cure others initiators non-CQ continued in this generation [4].

Despite of the highest light power of 2nd generation LED, the cure of materials using others photoinitiators is compromised. Thus, in third generation LED the manufacturers incorporated different wavelengths chips, which permit effective curing for not only CQ initiator and sufficient irradiance [4].

Light-curing protocols

In the conventional curing protocol a constant irradiance is used along the polymerization of light-activated materials. However, these materials show post-gel shrinkage and some curing methods were developed [15,16]: (1) pulse delay polymerization consists in a short flash of light initially followed by a waiting time of several minutes before of the final cure; (2) soft-start curing method uses a pre-polymerization at low-intensity light followed by a final cure at high intensity; and (3) in the ramp mode a gradual increase of light power is performed during the polymerization time. Some LCUs has this curing mode pre-programed or it can be carried out with conventional device by the increase of distance between the light guide tip from material irradiated, thus the approximation of the tip gradually increase the irradiance.

These alternative light-curing protocols aimed to increase pre-gel phase of resin-based materials by the slow cure, to reduce polymerization contraction due to stress relief, and final time of cure with high light power, to obtain adequate C=C conversion rate. However, it is reported that slow cure promotes few centers of polymer growth, which will result in a more linear polymer structure with relatively few crosslinks, more susceptible to degradation to food

substances and enzymatic attack.

On the other hand, it is related that rapid cure results in a multitude of growth centers, and consequently a polymer with higher crosslink density content [17]. However, the fast cure increases the viscosity of the system and reduces the molecular mobility, which promotes auto-deceleration of the polymerization reaction [18]. Thus, LCUs with irradiance extremely low and high is not recommended to reach adequate conversion rate and formation of a polymer structure with physical properties.

Problems related to polymerization reaction

An inherent problem of resinous materials is the polymerization shrinkage, which range from 2 to 5 vol% [19]. Furthermore, a significant proportion of unreacted monomer due the incomplete conversion of monomer into polymer is reported [17].

However, the increase on monomer conversion promotes higher shrinkage strain and, consequently, resultant stress at tooth-restoration interface, increasing the likelihood of mechanical failure, which it permits the ingress of bacteria causing pulpal irritation. In addition, stress may result in cuspal deflection, enamel microcrack propagation, and enamel fracture [19].

Different incremental composite placement techniques [20], light-curing protocols, and intermediate layer with hybrid glass ionomer or flowable composite [21] were proposed in the attempt to decrease the shrinkage stress effects and, consequently, resulting in lower clinical failure rate of resin-based restorations.

Constant researches with modification on the formulations of organic matrix chemistry have been performed to reduce polymerization shrinkage; such as silorane monomer developed from the reaction of the oxirane and siloxane molecules [19], dimer-acid chemistry derived monomers [22], resin contains a polymerization modulator [23], and others.

Silorane is a new monomer system, its polymerization occurs by a cationic reaction by the ring opening of oxirane moiety instead of free radical cure of conventional methacrylate composite resins, resulting on the lower contraction [24]. Others methacrylate-based composites decreased the shrinkage by modification on the monomer matrix, as introduction of dimer acid dimethacrylate monomers as diluent co-monomers [22] and chemical incorporation of a polymerization modulator in the center of the light curable resin backbone [22].

Conclusion

The polymerization reaction is directly related to improve the physical and chemical properties of curable materials. Therefore, an adequate conversion rate is strongly influenced by polymerization technique used and fundamental to clinical success of resinous materials longevity.

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