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Release of dibenzoyl peroxide from polymethyl methacrylate denture base resins: An in vitro evaluation

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ABSTRACT

Objectives. Dibenzoyl peroxide (BPO), an initiator in polymethyl methacrylate denture base resins, has been associated with allergic reactions in human patients. This study evaluated the content of BPO in acrylic denture base materials (ADBMs) prior and subsequent to recommended and additional post-polymerization, and subsequent to storage in varying solutions. The goal was to determine differences in BPO content in ADBMs, to determine whether differences are seen in BPO release over time and to test different procedures for additional BPO reduction.

Methods. Three heat-polymerizing, two auto-polymerizing and a microwave polymerizing “hypoallergic” ADBM were investigated. Five samples (Ø414.57 mg) were polymerized according to manufacturers’ instructions from each of the six acrylic resins for each of the variables to be investigated. For each material the BPO content was measured as delivered by the manufacturer and subsequent to recommended and post-polymerization protocols. The BPO content was also evaluated after storage in distilled water (22 °C, 192 h), in artificial saliva (35 °C, 192 h), in ethanol, potassium permanganate and ammonium ferric(II) sulfate solutions (22 °C, 48 h).

Results. High performance liquid chromatography (HPLC) and indirect iodometry were used to detect BPO concentrations. Significant differences were noted in BPO concentrations between the polymers as delivered from the manufacturer (0.13–1.20%), subsequent to polymerization (0.05–0.32%) and to the various treatment and storage procedures (H and U-tests, $p < 0.05$). The microwave polymerizing ADBM contained the lowest initial level of BPO. No reduction of BPO content was noted after 8 days of storage in artificial saliva or water. The most notable reduction (63–95%) occurred subsequent to post-polymerization cycles.

Significance. BPO was detected in all investigated ADBMs. It is unlikely, under oral conditions, that BPO is released from the investigated ADBMs. The BPO concentration can be reduced effectively by additional post-polymerization.

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1. Introduction

Subjective and objective complaints about acrylic resin dental prostheses are increasing [1]. Patients and dentists often assume that an allergic reaction to acrylic resin is responsible for these concerns. The result is often extensive and unsuccessful treatment [2,3]. In addition to residual monomer, dibenzoyl peroxide (BPO), has been linked to unfavorable tissue reactions to denture base acrylic resins [1,4]. BPO, although a strong irritant and potential sensitizer, is an organic compound commonly used as an initiator in the polymerization of dental acrylic resins [5–7]. No concentration threshold value for the initiator BPO is provided in the ISO standards, however the BPO concentration in acrylic resin powders is reported to be 0.2–1.28% [8,9].

Information on the BPO content of acrylic resins subsequent to polymerization is scarce [7,10]. Complete consumption of the initiator during the polymerization process has been assumed [1], however other authors suggest residual initiator is present in the polymerized resin [8,11]. Smith [8] found less than 0.05% BPO in acrylic resin polymerized for 6 h at 100 °C and approximately 400 h at 70 °C, respectively. This polymerization time substantially exceeded the recommended polymerization time [8] and the conclusion was therefore that a measurable residual of BPO would always be evident. Apart from these studies, the general discussion of this topic in the relatively old literature seems inconsistent and largely speculative. Equally controversial is the issue of possible peroxide remnants in the oral environment [3,6]. Smith [11] found a concentration of 0.57% BPO in an acrylic denture after 300 days of wearing, but did not state the initial BPO concentration directly after polymerization. Because of a possible influence of physiologically active substances in saliva on the release of soluble resin components, BPO could be set free and pose a risk for allergic reactions [3,12]. Articles on that topic report methods to reduce the BPO concentration in denture base acrylic resin materials [3,13]. Authors refer to the similarity of BPO with remnant monomer in acrylic resins. A common suggestion for the reduction of possible remnants after polymerization is to store the dentures in water for up to 8 days [13], although this has not yet been evaluated. The rationale for this regime was the fact, that the majority of the residual monomer got dissolved within the first week of storage in water [13]. Several methods for the reduction of BPO remnants would therefore seem possible: (a) storage in ethanol as an organic solvent to extract BPO (stronger solvents might destroy the material) [14], (b) storage in potassium permanganate or ammonium ferric(II) sulfate solution as these substances are used in the chemical industry to reduce the concentration of peroxides in chemicals [15], and (c) post-polymerization, as BPO is thermally unstable [6,11], and its half-life period shortens in a non-linear fashion as the temperature increases [14]. Storage in potassium permanganate or ammonium ferric(II) sulfate solutions for up to 48 h have been also suggested as methods for the reduction of monomer remnants in acrylic dentures [7,16]. Each of the methods suggested to reduce BPO concentrations in acrylic resins requires evaluation to confirm their influence.

This study was undertaken for three reasons. Firstly, to confirm the BPO concentration of representative and frequently used denture base acrylic resins both before and after polymerization recommended by the manufacturers. Secondly, a new and according to the manufacturer “hypoallergic” BPO free resin was to be examined. Thirdly, the release of BPO under simulated conditions was to be evaluated. In addition, possible methods for reducing the BPO concentration after polymerization may be identified.

2. Materials and methods

Three heat-polymerizing and two auto-polymerizing acrylic resins were examined. According to the manufacturer BPO is used as the polymerization initiator in all five of these acrylic resins. In addition, a “hypoallergic” microwave polymerizing resin was examined (Table 1). This acrylic resin is according to the manufacturer, a peroxide-free dimethacrylate. There may be a small amount of BPO in the source polymer. But this residual amount of BPO should not be detectable after microwave polymerization. According to the respective manufacturers all other tested resins contained BPO as initiator in the promoting system. The presence of other peroxides was not reported.

Heat- and auto-polymerizing resins were provided as powder and liquid or in dosage cartridges (SR-Ivocap). The microwave polymerizing dimethacrylate (Microbase) was supplied as a one component paste. All tested acrylic resins were polymerized according to the manufacturers' recommendations (Table 2). For SR-Ivocap, PalaXpress and Microbase an extended injection press method was used, for Paladon 65, Kallocryl A and Kallocryl B the conventional flask method [7] was used. After deflasking and superficial cleaning and smoothing, the specimens were sectioned with a water cooled dental diamond cutting disk into specimens 2 mm × 2 mm × 2 mm in size. The intent was to provide a large surface for the solvents to act upon. Care was taken to prevent the acrylic resins from overheating during this process to avoid modifying the concentration of the thermally unstable BPO.

For qualitative determination of BPO content in the samples, gel permeation chromatography (GPC) was utilized. It is a chromatographic method in which the molecular weight distribution of organic-soluble polymers is analyzed based on their hydrodynamic volume and by using an organic solvent as a mobile phase [3,9,17–19]. Samples of all acrylic

Table 1 – Denture base acrylic resins tested in study

Material	Type of polymerization	Manufacturer
Paladon 65	Heat-polymerizing	Heraeus Kulzer Inc., South Bend, Ind
SR-Ivocap	Heat-polymerizing	Ivoclar Vivadent, Amherst, NY
Kallocryl B	Heat-polymerizing	Speiko Ltd., Muenster, Germany
Microbase	Microwave-oven-polymerizing	Dentsply Intl, York, Pa
PalaXpress	Auto-polymerizing	Heraeus Kulzer Inc.
Kallocryl A	Auto-polymerizing	Speiko Ltd.

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