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Chemical characterization and bioactivity of epoxy resin and Portland cement-based sealers with niobium and zirconium oxide radiopacifiers

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ABSTRACT

Objective. The purpose of this study was to characterize and to evaluate the bioactivity potential of experimental root canal sealers (ES) based on Portland cement, epoxy resin with nano- and micro-particles of niobium or zirconium oxide used as radiopacifiers in comparison to AH Plus and MTA Fillapex.

Methods. Specimens of the sealers (10 mm in diameter × 1 mm thick) were prepared and the radiopacity was evaluated according to ISO 6876 (2012) specifications. Characterization of the sealers was performed under the scanning electron microscope (SEM) immediately after setting and after immersion for 28 days in Hank's balanced salt solution (HBSS). In addition X-ray energy dispersive spectroscopy (EDS), X-ray diffraction (XRD) and Fourier transform infrared (FT-IR) spectroscopy were also performed. The pH and calcium ion release were measured after 1, 7, 14, 21 and 28 days after completion of seating using a digital pH meter and an atomic absorption spectrophotometer, respectively.

Results. The experimental sealers exhibited an average radiopacity of 2.5 mm thickness of aluminum, which was similar to MTA Fillapex ($P > 0.05$) and inferior to AH Plus ($P < 0.05$). AH Plus did not show bioactivity. Although the experimental sealers did not exhibit the formation of hydration product, they encouraged the deposition of crystalline spherical structures of calcium deficient phosphate. The highest pH and calcium release values were observed with the experimental sealers ($P < 0.01$). ES-Nb-micro was the only sealer to present hexagonal shaped crystal deposition.

Significance. Novel root canal sealers based on a mixture of Portland cement, epoxy resin and radiopacifier exhibited a degree of bioactivity although no evidence of cement hydration was demonstrated on material characterization. The radiopacifier particle size had limited effect on the sealer microstructure and chemical properties.

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1. Introduction

Bioactivity can be defined as a beneficial effect produced by some materials when they are implanted in living tissues. Through biochemical and biophysical reaction, the tissue fluid interacts with these materials leading the formation of carbonated apatite crystals, which are the main mineral phase of hard tissues, such as bone, dentin and cementum [1]. Ideally, root canal sealers and root-end filling materials should be bioactive since they are in directly contact with periapical tissues through the root apex.

Mineral trioxide aggregate (MTA) is used extensively in Dentistry mainly as reparative cement in cases of root perforation [2], pulpotomies [3] and as a root-end filling material [4] due to its biological properties. MTA induces hard tissue deposition, and is thus bioactive [1,5–7]. The bioactivity results from the reaction of the calcium hydroxide produced during the hydration of the Portland cement component with phosphates present in tissue fluids [8]. Most root canal sealer cements do not possess any bioactivity. MTA Fillapex (Angelus, Londrina, Brazil) which is a sealer based on MTA, was reported to exhibit bioactivity when in contact with simulated tissue fluids in human cell culture [9].

MTA and Portland cement mixed with water, results in a granular and sandy paste with unfavourable handling characteristics that precludes the use of MTA as a root canal sealer [10]. Therefore, a number of studies have been performed attempting to develop a root canal sealer based on MTA [11–20] or tricalcium silicate [21–23], which is the main constituent phase in MTA. MTA Fillapex is composed of MTA and other compounds, such as resins, that result in an endodontic material with adequate physicochemical properties to be used as sealer [24]. Since MTA and Portland present a similar chemical composition [25] and biological response [26], an experimental root canal sealer (MTA Sealer), containing white Portland cement, a radiopacifying agent (zirconium oxide), an additive (calcium chloride) and a resinous vehicle, which conferred viscosity to the sealer, have been developed and its physicochemical and biological properties showed promising results [17,20].

The role played by radiopacifying agents in the bioactivity of the endodontic materials is still not well reported. Bismuth oxide is the radiopacifying agent present in MTA Fillapex and some studies have shown that this material in general, negatively affects the physico-chemical [27,28] and biological properties [29,30] of MTA cements. Furthermore bismuth oxide has been implicated with tooth discoloration by interacting with collagen present in dental hard tissues [31] and also reacting with sodium hypochlorite used routinely during endodontic therapy [32]. To avoid the side effects caused by bismuth oxide, alternative radiopacifying agents have been proposed [33–38]. Replacement of bismuth oxide with zirconium oxide resulted in a material with physicochemical properties comparable to the commercial version that contained bismuth oxide [39,40]. Furthermore, this material was shown to be bioactive since it induced the deposition of precipitates that precedes apatite formation when in contact with simulated body fluid [40].

Niobium is a transition metal that can also be added to root canal sealers to enhance radiopacity. Niobium oxide increased the radiopacity of methacrylate-based root canal sealers [41]. Also, the oxidized form exhibited biocompatibility and ability to enucleate hydroxyapatite when it was used to cover dental implants [42].

The purpose of this study was to characterize and evaluate the bioactivity potential of experimental root canal sealers based on Portland cement and an epoxy resin incorporating nano and micro particles of niobium or zirconium oxide radiopacifiers and compare these novel sealers to AH Plus and MTA Fillapex.

2. Methodology

The materials used in this study included a range of conventional and experimental (ES) root canal sealers:

- AH Plus (Dentsply International, Addlestone, UK);
- MTA Fillapex (Angelus Dental Solutions, Londrina, SP, Brazil);
- ES-Zr-micro (Araraquara Dental School, São Paulo State University, Brazil) composed of a mixture of Portland cement, micro-sized zirconium oxide (Sigma–Aldrich, St Louis, MO) and an epoxy resin;
- ES-Zr-nano (Araraquara Dental School, São Paulo State University, Brazil) composed of a mixture of Portland cement, nano-sized zirconium oxide (Institute of Physics of São Carlos, University of São Paulo, São Carlos, Brazil) and an epoxy resin;
- ES-Nb-micro (Araraquara Dental School, São Paulo State University, Brazil) composed of a mixture of Portland cement, micro-sized niobium oxide (CBMM, Companhia Brasileira de Metalurgia e Mineração, Araxá, MG, Brazil) and an epoxy resin;
- ES-Nb-nano (Araraquara Dental School, São Paulo State University, Brazil) composed of a mixture of Portland cement, nano-sized niobium oxide (Institute of Physics of São Carlos, University of São Paulo, São Carlos, Brazil) and an epoxy resin.

The radiopacifiers replaced 30 wt% of white Portland cement (Portland Cement; CPB-40; Votorantin Cimentos, Camargo Correa S.A., Pedro Leopoldo, MG, Brazil). The microparticles of niobium and zirconium oxide were purchased from companies manufacturing chemicals. The nanoparticles of niobium and zirconium oxide were prepared by the polymeric precursor method. The zirconium oxide supports were prepared from the precursor salt $ZrO(NO_3)_2{\cdot}xH_2O$ (Alfa Aesar). Aqueous solutions of this salt were prepared, mixed and added to an aqueous solution of citric acid (held at 60 °C), with constant stirring. Subsequently, ethylene glycol ($HOCH_2CH_2OH$) was added to polymerize the citrate by a polyesterification reaction (at 120 °C). The citric acid:metal molar ratio was 3:1, while the citric acid:ethylene glycol mass ratio was 60:40. The resulting polymer resin was then calcined at 300 °C for 4 h, and the after 600 °C/2 h to produce ZrO_2 crystalline particles. Whereas to produce niobium oxide nanoparticles, an aqueous solution of niobium ammonium