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ScienceDirect
Acta Biomaterialia 4 (2008) 432–440
Acta BIOMATERIALIA
www.elsevier.com/locate/actabiomat

Effects of incorporation of hydroxyapatite and fluoroapatite nanobioceramics into conventional glass ionomer cements (GIC)

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Received 21 May 2007; received in revised form 4 July 2007; accepted 30 July 2007
Available online 25 August 2007

Abstract

Hydroxyapatite (HA) has excellent biological behavior, and its composition and crystal structure are similar to the apatite in the human dental structure and skeletal system; a number of researchers have attempted to evaluate the effect of the addition of HA powders to restorative dental materials. In this study, nanohydroxy and fluoroapatite were synthesized using an ethanol based sol–gel technique. The synthesized nanoceramic particles were incorporated into commercial glass ionomer powder (Fuji II GC) and were characterized using Fourier transform infrared and Raman spectroscopy, X-ray diffraction and scanning electron microscopy. Compressive, diametral tensile and biaxial flexural strengths of the modified glass ionomer cements were evaluated. The effect of nanohydroxyapatite and fluoroapatite on the bond strength of glass ionomer cement to dentin was also investigated. Results showed that after 1 and 7 days of setting, the nanohydroxyapatite/fluoroapatite added cements exhibited higher compressive strength (177–179 MPa), higher diametral tensile strength (19–20 MPa) and higher biaxial flexural strength (26–28 MPa) as compared with the control group (160 MPa in CS, 14 MPa in DTS and 18 MPa in biaxial flexural strength). The experimental cements also exhibited higher bond strength to dentin after 7 and 30 days of storage in distilled water. It was concluded that glass ionomer cements containing nanobioceramics are promising restorative dental materials with both improved mechanical properties and improved bond strength to dentin.

Keywords: Glass ionomer cement; Nanohydroxyapatie; Nanofluoroapatite; Sol–gel synthesis; Mechanical properties

1. Introduction

Glass ionomer cements (GIC) were invented by Wilson et al. at the Laboratory of the Government Chemist in 1969 [1,2]. These materials are water-based cements, and are also known as polyalkenoate cements [3]. They are based on the reaction between an alumino-silicate glass and polyacrylic acid, and cement formation arises from the acid–base reaction between the components [4,5]. The glass ionomer name is derived from the formulation of the glass powder and the ionomer that contains carboxylic acids. These cements are adhesive to tooth structure and translucent [6–8]. The matrix of the set cement is an inorganic–organic network with a highly cross-linked structure. The first glass ionomer cement (GIC) introduced had the acronym "ASPA", and comprised alumina-silicate glass as the powder and polyacrylic acid as the liquid. This product was first sold in Europe (De Trey Company and Amalgamated Dental Company) and later in the USA [9–11]. Glass ionomer cements have desirable properties, such as adhesion to moist tooth structure and an anticariogenic action (due to fluoride release). In addition, the coefficient of thermal expansion for glass ionomers is close to that of

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1742-7061/$ - see front matter
doi:10.1016/j.actbio.2007.07.011

tooth structure and they are biocompatible. Because of these unique properties, GICs are very useful and important as dental restorative materials [12–15]. In addition to their advantages, GICs suffer from the disadvantage of being brittle. Significant improvements have been made since the invention of GIC and are continuing to be made to enhance the physical properties of the cements. Although stronger and more aesthetic materials with improved handling characteristics are now available, lack of strength and toughness are still major problems [1–19].

Since hydroxyapatite (HA) has excellent biocompatible properties, and a composition and crystal structure similar to apatite in the human dental structure and skeletal system, a number of studies have tried to evaluate the effect of the addition of HA powders to restorative dental materials such as GICs [20–25]. Hydroxyapatite is a type of calcium phosphate, which is the main mineral component of the enamel of the tooth; it also comprises more than 60% of tooth dentine by weight. In addition, HA comprises the inorganic matrix of human bone in the form of phosphocalcic hydroxyapatite, which has the following formula $Ca_{10}(PO_4)_6(OH)_2$ and contains both phosphate and hydroxyl ions. The ability of HA to integrate with bone structures can help bonding between bone and implant structures and also support bone ingrowth without breaking down or dissolving [20,21].

GICs have been found to interact with HA via the carboxylate groups in the polyacid. Therefore, the incorporation of HA into GICs may not only improve the biocompatibility of GICs, but also have the potential of enhancing the mechanical properties. In addition, it has the ability to increase the bond strength to tooth structure due to its similar composition and structure to enamel and dentin. Lucas et al. [22,23] reported that the addition of the HA particles to the glass ionomer powder has the ability to increase the fracture toughness of the cement, which maintained long-term bond to dentin. Furthermore, they reported that the addition of HA did not hamper continued fluoride release and also maintained long-term bond strength to dentine. In addition, Gu et al. reported that GICs containing 4 wt.% HA particles exhibited enhanced mechanical properties in comparison with commercial GICs [24,25].

It is envisaged that the presence of HA and fluoroapatite (FA) nanoceramics in the GIC matrix have the ability to increase the mechanical and bond strength of the resulting material. Hence, the main aim of this study was to synthesize HA and FA nanoparticles and to assess the effect of their addition on the mechanical properties and bond strength to dentin of conventional GICs. Fuji II conventional GIC was used as the control group in this study due to its availability and popularity in dental communities; however, in next steps of these series of experiment the effects of addition of nanoceramics on properties of stronger and modern GICs such as Fuji IX and Ketac Molar will be investigated.

2. Materials and methods

2.1. Materials

The glass powders and all the liquids used in the experiments were of commercial grade, obtained from Fuji II (GC International, Tokyo, Japan). All the other chemicals in this study were of analytical grade and applied as received from Sigma–Aldrich Chemical Co. Calcium nitrate tetrahydrate [$Ca(NO_3)_2 \cdot 4H_2O$], $(NH_4)_2HPO_4$, ammonium fluoride (NH_4F), ethanol (C_2H_5OH) and ammonium hydroxide (NH_4OH) were used as obtained.

2.2. Synthesis of nanohydroxyapatite and nanofluoroapatite

Nanohydroxyapatite was produced by an ethanol-based sol–gel method similar to those of Kuriakose et al. [26] and Feng et al. [27].

Initially 6.6 g (50 mmol) of $(NH_4)_2HPO_4$ was dissolved in 50 ml of ethanol. In the second step, 19.702 g (84 mmol) of Ca $(NO_3)_2 \cdot 4H_2O$ was dissolved in 50 ml of ethanol in order to make a 0.5 M solution. This solution was added dropwise to the initial solution using a dropping funnel at the rate of 5 ml min^{-1}. The reaction was carried out at a constant temperature of 85 °C for 4 h. During the reaction, the pH of the solution was maintained at 10 by the dropwise addition of NH_4OH solution (up to a total amount of 5 ml).

For FA synthesis, the method described by Cavalli et al. [28] was adopted. In the experimental procedure initially 6.6 g (50 mmol) of $(NH_4)_2HPO_4$ was dissolved in 50 ml of ethanol, then 19.702 g (84 mmol) of $Ca(NO_3)_2 \cdot 4H_2O$ was dissolved in 50 ml of ethanol in order to make a 0.5 M solution. Subsequently, 0.62 g (16.7 mmol) of NH_4F with an appropriate molar ratio (Ca:P:F = 3:5:1) was added to the above solution as the source of fluoride ion. This solution was added dropwise to the initial solution using a dropping funnel at the rate of 5 ml min^{-1}. The reaction was carried out at a constant temperature of 85 °C for 4 h.

The nanopowders produced were dried using a freeze dryer (Wizard 2.0 SP Industries Co. The Virtis Company, NY). The powder samples were heat treated in a Carbolite® (Sheffield, UK) furnace. The samples were heated up to 400 °C at a rate of 10 °C min^{-1} and held at this temperature for 2 h, then heated at the same rate up to 800 °C and held for another 2 h at this temperature. Upon cooling, the powders were gently ground manually for 10 min using a mortar and pestle. The yields of each synthesis reaction were calculated and are tabulated in Table 1.

Table 1
Yield of synthesized HA and FA

Material	Yield (%)
Hydroxyapatite	78
Fluoroapatite	69

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