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Synergic effect of chitosan and dicalcium phosphate on tricalcium silicate-based nanocomposite for root-end dental application

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ABSTRACT

In recent years, cement composites based on calcium silicate have been more generally considered for medical applications. Calcium silicate Cement are among the categories that are used in dental root canal treatment. The aim of this study is to make new calcium silicate cement with dicalcium phosphate and chitosan additives to preserve and strengthen desirable properties of this type of cements. In this study, composite dental cement based on calcium silicate was prepared. Then effect of adding biodegradable and biocompatible polymer such as chitosan on setting properties and its structure were studied. In this study, a combination of calcium silicate, dicalcium phosphate (DCP) and bismuth oxide (Bi_2O_3) as powder phase and 2% solution of the chitosan dissolved in 1% acetic acid solution as liquid phase, was used. As well as control sample was obtained by mixing the powder with distilled water as the liquid phase. Based on the obtained results, setting time of composite cement was changed from 51 to 67 minutes by adding chitosan polymer. Presence of chitosan also reduced the compressive strength a little. The bioactivity of the cement were studied in a solution of simulated body fluid (SBF) for 14 days. The samples were analyzed by SEM to identify the microstructure and by XRD to determine crystal structure. The composition of cement before incubation in SBF was included early phases (phase calcium silicate and calcium phosphate) that after 14 days of immersion in SBF, they were converted to layer-shaped hydroxy apatite and the presence of chitosan had not any influence on the final phase of hydroxy apatite.

1. Introduction

Today, advanced materials such as nanostructured materials [1,2], hybrid materials [3] and engineered polymeric materials [4,5] have become widely used in various applications such as gene delivery [6], optogenetics [7], anti-bacterial materials [8], extraction of proteins from natural resources [9], photodynamic therapy [10] and endodontics [11].

An ideal endodontic material would cohere to tooth structure, maintain an adequate seal, stable, radiopaque, and be insoluble in tissue fluid exhibiting biocompatibility [12,13]. A number of materials such as amalgam, composite resin, and glass-ionomer cements have been developed for fillings and puncture repair [14]. Unfortunately, none of these materials have been assure the total requirements of an ideal material [15].

Mineral trioxide aggregate (MTA), a biomaterial investigated for endodontic applications, is a mechanical mixture of three ingredients including Portland cement (75%), bismuth oxide (20%), and gypsum (5%) and trace amounts of SiO_2, CaO, MgO, K_2SO_4 and Na_2SO_4 [16]. The components of Portland cement are dicalcium silicate, tricalcium silicate, tricalcium aluminate, and tetracalcium aluminoferrite. The MTA prepared as a mixture of powder and water is used in a slurry form, which gently tightens in the oral environment [17]. MTA exposed to synthetic tissue fluid (such as simulated body fluid, SBF) at 37 °C delivers its metallic constituents and make precipitates with a composition structure similar to hydroxyapatite ($Ca_{10}(PO_4)_6(OH)_2$, HA) [18].

The HA has a same chemistry as the minerals of a human skeleton, meaning that it is biocompatible and osteoconductive [19]. It was reported that calcium phosphate cement (CPC) consisted of dicalcium phosphate dihydrate (DCPD) and tetracalcium phosphate (TeCP) hardens himself to form hydroxyapatite. So that, it seems that adding a component of calcium phosphate cements such as dicalcium phosphate to MTA can promote formation of HA phase in MTA [20].

The chitosan, a linear polysaccharide, composed of glucosamine and *N*-acetyl glucosamine, is one of the most plentiful natural polysaccharides, captured from chitin by deacetylation. It is degradable, biocompatible, antibacterial and non-toxic, which makes it noteworthy for drug delivery system [21] and clinical uses [22]. As reported, the presence of chitosan in cement components decreases dramatically setting time besides persuading antibacterial property [23].

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According to our best knowledge in literature, adding dicalcium phosphate and chitosan to MTA including Portland cement and bismuth oxide has not been reported, yet. In this work, we utilized dicalcium phosphate in MTA-like cement (Portland cement and bismuth oxide) and compare hardening behavior in pure water and aqueous chitosan solution. It was shown that incorporating chitosan and dicalcium phosphate in MTA endue anti-microbial property and rapid formation of apatite film to cement nanocomposites to aim more biocompatible with root-end tissue.

2. Materials and methods

2.1. Materials

In this study, the cement consisted of three powder components admixed a liquid part including pure water and chitosan solution. Three powder components are included white Portland cement (PC) clinker (Saveh company, Iran, detailed composition in Table 1), bismuth oxide (Bi_2O_3, Merk) and dicalcium phosphate (DCP) (Ca_2HPO_4, Merk).

The liquid component was a solution of chitosan and acetic acid. The chitosan (Medical-grade, degree of deacetylation (DD) = 94%, Mv = 830,000 Da) was purchased (Chitotech company, Iran). The mass fraction of chitosan was 2% in liquid phase. After parallel experiments, four types of liquid components were chosen in this research to investigate the effects of the concentration of acetic acid on mechanical properties and bioactivity. The composition of the liquid phase is shown in Table 2.

2.2. Fabrication of cements

Powder cement was prepared by mixing PC clinker, Bi_2O_3 and DCP with chitosan aqueous solution in a fast mill (Fast mill FMD-2 Model, Sanatceram, Iran). The mean particle size of cement powder was Less than 44 μm (measured using the Brookhaven laser particle analyzer, BI200SM, USA) after milling for 5–7 h. The chitosan solution was made by dissolving 2 wt% chitosan in a 1% acetic acid solution. 18 samples were made by dissolving three composition types of powders in two solution type with three times repeating (mentioned in Table 2). In this study, the liquid/powder ratio (L/P) of this cement samples was set at about 0.28 ml/g. The six types of cement were named as mentioned at Table 2.

2.3. Setting time measurement

Each Sample of six types of cement was molded into cylindrical mold with 12 mm in diameter and 5 mm in length. Setting time of these cements were measured by using the Gilmore needle method according to ISO standard 9917 that used to dental cement. A cement specimen kept in 98% relative humidity at 37C, was considered set when a 400-g mass loaded to a needle with a tip diameter of 1 mm failed to make a perceptible circular indentation on the surface of the cement.

Table 1
Composition of used Portland cement.

Chemical Properties	White Clinker (%)
SiO_2	24.30
Al_2O_3	4.60
Fe_2O_3	0.45
CaO	65.70
MgO	2.70
SO_3	0.50
Na_2O	0.30
K_2O	0.38

Table 2
Chemical composition of produced cement composites.

Powder component	Liquid component: Distilled water	Liquid component: 2% chitosan solution
20% Bi_2O_3 + 80% Clinker	$B_{20}C_{80}W$	$B_{20}C_{80}Ch$
20%Bi_2O_3 + 15% DCP + 65% Clinker	$B_{20}D_{15}C_{65}W$	$B_{20}D_{15}C_{65}Ch$
20%Bi_2O_3 + 30% DCP + 50% Clinker	$B_{20}D_{30}C_{50}W$	$B_{20}D_{30}C_{50}Ch$

2.4. Compressive strength of cements

The compressive strength of the samples were measured by universal Testing Machine (SANTAM) with crosshead speed 1 mm/min. The compressive strength was calculated by using the fracture load divided by the specimen's cross-sectional area. Three replicates were carried out for each group of materials and the results were expressed as mean ± standard deviation.

2.5. Morphology observation of cements

After setting cement samples at room temperature for 30 days, they were observed by a scanning electron microscope (SEM-KYKY- Model: 3200EM - TE-SCAN – MIRA3) to illustrate the morphology of the produced samples under various synthesis condition.

2.6. X-ray diffraction analysis

The lattice structure and phase composition were analyzed by X-ray diffraction (Siemens D-500, 40 kV, 20 mA) analysis of 18 samples before and after immersion in SBF solution.

2.7. FTIR analysis

Infrared spectroscopy (FTIR-BRUKER-Model: TENSOR27-Germany) with wave number 400–4000 cm^{-1} in transmission mode identified the existence of organic functional groups on surface of cement nanocomposites.

2.8. Atomic absorption analysis

Atomic absorption spectroscopy (AAS, PerkinElmer, USA) was used to identify the concentration of Ca^{2+} ions in simulated body fluid after soaking the cement samples.

2.9. pH measurements

The pH of the soaking solutions was collected after 28 days and measured using a pH meter (equipped with a Hamilton liq-glass electrode and ±0.01 resolution). It was calibrated with acidic–neutral–alkaline standard solutions.

2.10. Soaking in simulated body fluid (SBF)

To investigate the bioactivity of the six types of cement, cylindrical samples (5 mm × 12 mm) were soaked in 50 ml of simulated body fluid (SBF) and incubated at 37 °C with pH = 7 for 28 days. After the preselected of samples, the disks were gradually washed with deionized water to remove SBF solutions followed by drying at room temperature. The concentrations of Ca^{2+} and in the SBF solution after 28-day soaking and pH value of the soaking solution were determined by atomic absorption spectroscopy (AAS) and an electrolyte-type pH meter, respectively. The SBF was not changed daily when the concentrations of Ca^{2+} ions were being measured.