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Development of nanosilica bonded monetite cement from egg shells

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ABSTRACT

This work represents further effort from our group in developing monetite based calcium phosphate cements (CPC). These cements start with a calcium phosphate powder (MW-CPC) that is manufactured using microwave irradiation. Due to the robustness of the cement production process, we report that the starting materials can be derived from egg shells, a waste product from the poultry industry. The CPC were prepared with MW-CPC and aqueous setting solution. Results showed that the CPC hardened after mixing powdered cement with water for about 12.5 ± 1 min. The compressive strength after 24 h of incubation was approximately 8.45 ± 1.29 MPa. In addition, adding colloidal nanosilica to CPC can accelerate the cement hardening (10 ± 1 min) process by about 2.5 min and improve compressive strength (20.16 ± 4.39 MPa), which is more than double the original strength. The interaction between nanosilica and CPC was monitored using an environmental scanning electron microscope (ESEM). While hardening, nanosilica can bond to the CPC crystal network for stabilization. The physical and biological studies performed on both cements suggest that they can potentially be used in orthopedics.

1. Introduction

The paper is an effort to develop orthopedic cements from cheap raw materials such as egg shells, a waste product from the poultry industry. The paper draws motivation and experience from our on-going effort on the development of novel orthopedic cement compositions [1–3]. Specifically, we have developed a monetite (DCPA, $CaHPO_4$) based cement bonded with silica to improve bioactivity [4]. An interesting feature of this cement is that there is significantly reduced exothermicity of the compositions during setting. This feature was obtained using a microwave pre-treatment. The benefits of the present work are several: 1) the effort facilitates waste disposal; 2) abundant supply of starting materials can significantly bring down the manufacturing costs; and 3) naturally derived starting powder should contain other elements, mimicking the human bone mineral in composition. Realizing these advantages, various groups in the world are working on egg-shell derived calcium phosphates and reporting interesting results. In spite of these activities over more than a decade, very little effort is directed towards their applications. Hence is this effort. To introduce this topic, perhaps it is worthwhile here to provide a critique of the previous efforts.

In a recent review on natural source derived calcium phosphates, Akram et al. classify natural sources as osseous, botanical and biogenic in origin [5]. Egg shells belong to the biogenic sources [5]. Generally egg shells comprise of five different structural layers going from the inside to out, these are: shell membranes, mammillary layers, palisade layer, vertical crystal layer, and the cuticle [6]. Of these, $CaCO_3$ in calcite form is present in the mammillary layer, palisade layer and the vertical crystal layer. The mineral content of the chicken egg shell, for example, is 95% calcite with the rest consisting of proteins such as proteoglycans and glycoproteins [6].

Since 1999, egg shells have been used as a calcium source for the synthesis of calcium phosphates, most notably hydroxyapatite (HA, $Ca_{10}(PO_{4})_{6}(OH)_2$) [7–13]. The common approach in these efforts is to crush the egg shells, convert the calcite to calcium oxide via calcination and then treat the final compound with a source of phosphorus such as phosphoric acid [13], diammonium hydrogen phosphate [9] and sodium hydrogen phosphate [14]. It is interesting to note that microwave energy was used to synthesize powders to drive the reaction between as-prepared calcium sources with phosphates [9,10]. As discussed later, microwave energy is also used in the present work, albeit for different reasons. While all of these studies are interesting, the common drawback is that all of them are focused on the synthesis of HA. It is well known that HA itself has limitation of its poor resorbability. Second, after the synthesis is over, the powders need sintering at high temperatures for making samples. Finally, there have been only two reports in the literature that deal with the applications of egg-shell derived powders. Gouma et al. reported incorporating the egg-shell derived powders into electro-spun scaffolds for bone regeneration [14]. Zhang et al.,

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Table 1
Information of used nanosilica NexSil 125k.

Product	Particle size (nm)	Surface area (m^2/g)	wt.% SiO_2	pH @ 25 °C	Specific gravity	Particle charge
NexSil 125k	85	35	40	8.9	1.3	Negative

reported using the egg-shell derived HA powders in the detection of bisphenol A, a known carcinogen [15].

As mentioned in the beginning, our research is translatory in nature and our current state-of-the-art in the cement development is about a DCPA based self-setting cement composition, with no exothermicity during the setting [4]. DCPA has interesting properties as compared to its better known counterpart, brushite (DCPD, $CaHPO_4 \cdot 2H_2O$). Research on DCPA shows that: 1) DCPA has chemical composition, solubility, biocompatibility and osteoconductivity comparable to DCPD [16,17]; and 2) DCPA does not reprecipitate into apatite in vivo as compared to DCPD, thus providing greater possibility for enhanced resorption [18, 19].

The occurrence of exothermic reactions between calcium hydroxide ($Ca(OH)_2$) and phosphoric acid (H_3PO_4) during the setting of the DCPA cement [1–3], which may reduce the clinical effectiveness of this cement and limit some of its applications. To address the heat-generation problem, we developed a novel microwave assisted approach [20]. This technology uses microwave irradiation to temporarily stop the acid–base setting reaction common to alkaline earth phosphate cements. The resulting cement powders are preserved in an active precursor phase, which continues the setting reaction once exposed to a liquid phase again. It is worth emphasizing again that most of the heat generated in the cement setting comes from the acid–base reaction in the first few seconds. However, the microwave prepared cement powders are in the crystal nucleation and growth stage, a stage that exists after the exothermic process. This is the reason that, when exposed to a liquid phase again, almost no heat is generated. In addition to the reduction of heat generation during acid–base reaction, another advantage of this microwave assisted technique is the reduction of production cost. In conventional calcium phosphate cement compositions, the starting compounds such as tetracalcium phosphate (TTCP) and α-tricalcium phosphate (α-TCP) are required to undergo high temperature (>1000 °C) exposures for hours. This, significantly increases the cost of production. However, in this new microwave based system, no such high temperature exposure is needed, thus greatly reducing the energy consumption and the cost of production of cement powder. Finally, nanosilica sol is used to modify the cement characteristics. Silica in nanocrystalline powder form, an additive conventionally used for civil cement strengthening, is also applied in improving mechanical and biological performance of both synthetic bone and dental materials [21–23]. However, nanosilica sol is quite different from those applications. The concept of using nanosilica in biomedical cement originated from the dissolution products from bioactive glasses. The bioactive glasses release calcium and silicate content that leads to the up-regulation and activation of seven families of genes in osteoprogenitor cells and gives rise to rapid bone regeneration [24]. Additionally, in our previous work, we attempted to load nanosilica to DCPA cement via co-reaction during microwave irradiation, which improved the bioactivity [4]. Here we plan to combine nanosilica by co-mixing with as-prepared DCPA cement powder to further improve the strength of cement.

To recap, the objectives of this work are to develop an orthopedic cement composition using cheap raw materials derived from egg shells, an industrial waste. It is anticipated that unlike most of the previous reports on egg-shell derived starting materials, this work will produce an industrially relevant product. The utilities of this work are as follows: 1) ease in waste disposal; 2) development of a value-added product for biomedical applications; 3) use of simple technology without the use of high temperature exposure; 4) application of microwave pretreatment to avoid generation of high temperature during setting of the cement; and 5) addition of nanosilica sol to act as a bonding agent.

2. Materials and methods

All the chemical reagents were purchased from Fisher Scientific if not specifically noted. Egg shells were collected from eggs sold by Wal-Mart. Nanosilica was in a colloidal form (NexSil 125k, Nyacol Nano Technologies) and detailed information is shown in Table 1.

The surfaces of the collected egg shells were mechanically cleaned using ultra-sonication. They were subsequently calcined at 900 °C for 3 h to completely burn out organic materials and convert the major inorganic component $CaCO_3$ into CaO. After the powder cooled down, the calcined materials were crushed and ground in an agate mortar to get a fine powder (calcined egg shell). The synthesized powder was incubated in deionized (DI) water and then followed by filtering to convert the synthesized CaO into fine $Ca(OH)_2$ powder. This was also done to remove trace soluble salts from the powder. The prepared raw powder was dried at 60 °C in an oven for 24 h.

The solid powder phase for microwave treated DCPA bone cement powder (MW-CPC powder) was the synthesized $Ca(OH)_2$ containing raw powder. The liquid phase was a mixture of 6 g sodium bicarbonate ($NaHCO_3$), 13 ml phosphoric acid (H_3PO_4, 85%) solution and 2 ml deionized water. MW-CPC powder was prepared by manually mixing 1.9 g of raw powder into a mixture of 1.5 ml additional DI water and 3 ml liquid phase in an agate mortar using an agate pestle. After 1 min of mixing the

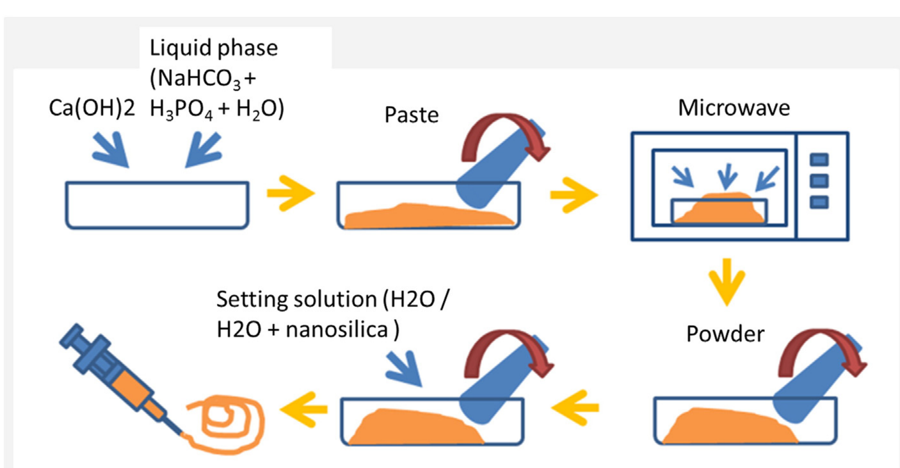

Fig. 1. Procedure of preparing CPC using microwave assisted technology.