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Mechanical and tribological properties of hydroxyapatite nanoparticles extracted from natural bovine bone and the bone cement developed by nano-sized bovine hydroxyapatite filler

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Abstract

The aim of this study is twofold. Firstly, it provides a nano-sized hydroxyapatite derived from bovine bone (BHA), as a raw material and natural source of HA, and to obtain the mechanical and tribological properties of sintered BHA ceramic. Secondly, it evaluates the mechanical and tribological properties of a commercially available bone cement by incorporating nano-sized BHA as a bone compatible nano-filler. In order to achieve these two goals, the mechanical and tribological properties of sintered BHA ceramic and nano-composite cements were measured using nano-indentation and nano-scratch experiments. The results indicated that the nano- hydroxyapatite of single phase with high crystallinity and appropriate mechanical and tribological properties could be produced from the natural bovine bone. Moreover, it was found that the nano-composite with 10 wt% BHA exhibited a good improvement in mechanical and tribological properties in comparison with other examined PMMA/BHA nano-composites.

Keywords: B. Nano-composite; C. Mechanical properties; Hydroxyapatite; Bovine bone; Bone cement

1. Introduction

In the past few decades, considerable research studies have been devoted to the synthesis of various bioceramics. Amongst different classes of bioceramics, hydroxyapatite (HA) [$Ca_{10}(PO_4)_6(OH)_2$] is the most emerging bioceramic, which is extensively used in various clinical applications such as orthopedics and dentistry. The intense use of HA has been due to its special chemical composition, and also its biological and crystallographic similarity with the mineral portion of hard tissues. There are two main methods for producing HA; the first is inorganic synthesis such as wet-chemical method, sol–gel method and hydrothermal method [1–6]. The other technique is the use of natural sources such as eggshells, cuttlefish shells and bovine bone as the main starting materials to synthesize HA [7–10]. Bovine bone, as a raw material, is a potential source of natural HA which can be a good choice for producing hydroxyapatite powder. This is because as an inexpensive and easily available material, bovine bone is morphologically and structurally similar to human's bone. However, the mechanical and tribological properties of HA obtained from natural sources, especially HA from bovine bone (BHA), have not been fully understood and investigations in this field are still widely open.

Polymethylmethacrylate (PMMA) polymers reinforced by Hydroxyapatite (HA) are among the useful applications of HA which have high potential for improving the biological and physicochemical properties of orthopedic cements. Acrylic or PMMA-based bone cements are widely used in clinical applications for bone cementation and fixation purposes of orthopedic prosthesis. The lack of strong adhesion between the

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implant and bone has prompted many investigations in which bone-compatible fillers are incorporated into the acrylic bone cement matrix. Researchers have found that the incorporation of hydroxyapatite into the bone cement matrix can improve the biocompatibility of cement and may also enhance fixation by directly stimulating the hosting bone [11–15]. Despite various potential applications of PMMA/HA composite, limited information is available on the mechanical and tribological properties of HA-reinforced bone cements, especially in the scope of nanomaterials. One of the main features of nano-sized particles is their high surface area to volume ratios. This allows the nanoparticles to provide substantially higher interfacial area for load transfer when incorporated into a composite matrix compared to their micro counterparts.

In this study, two main purposes were pursued; the first goal was to reach a nano-hydroxyapatite derived from natural bovine bone (BHA), as the raw material, and to explore the mechanical behavior of sintered BHA ceramic. The other aim was to evaluate the effect of BHA on the mechanical and tribological properties of the resulting PMMA/BHA nano-composite cements (as an important application of HA). In order to achieve these aims, the mechanical and tribological properties of BHA ceramic and nano-composite cements were measured using nano-indentation and nano-scratch experiments.

2. Materials and methods

2.1. Nano-hydroxyapatite powder preparation

The hydroxyapatite powder was derived from natural bovine bone. The purchased bovine bone was cleaned from visible adhered impurities and waste substances such as joint cartilage, ligaments and tissues stuck on the bone. The cleaned bone was boiled in distilled water for 3 h to make the removal of the bone marrow and tendons easier. After the cleaning process, the clean bone samples were defatted by continuing the boiling in the distilled water. The boiled bone samples were dried in an oven at 100 °C for 24 h in order to avoid soot formation on the surface of the material during the heating treatment. After that, dried specimens were cut into cubic prism shapes (10 mm × 10 mm × 10 mm) and calcined in an electric furnace at 900 °C using a temperature rate of 5 °C/min under ambient condition. The temperature was kept for 2 h in the same degree to remove the organic substances. The samples were cooled until they reach the room temperature by slow furnace cooling and then crashed by mortar pestle into powder. Hereafter, since the molecular purity and mechanical, physical and biological properties of HA are improved by nano-sized hydroxyapatite, the nano-structural powders were produced via a high energy planetary ball mill. Among this procedure, in order to minimize impurities during the milling step, a zirconia cup and balls with a ball-to-powder weight ratio of 6:1 were used.

2.2. Sintered BHA ceramic preparation

The BHA powder was uniaxially pressed in 156 MPa into the green body using a cylindrical die with a 20 mm diameter. The compacted green body was pressurelessly sintered in air atmosphere in temperature of 1200 °C, with a furnace ramp rate of 5 °C/min and dwell time for 2 h. It is worth noting that this temperature was selected based on the recommendations of the previous studies [16–18]. In order to obtain a smooth surface for nano-indentation and nano-scratch tests, the surface of sample was polished with a diamond paste having a mesh size of 1 and 0.5 μm, respectively and the roughness of the sample was checked using atomic force microscopy (AFM).

2.3. Nano-composite sample preparation

EUROFIX GUN® (Low viscosity, Synimed Company, France), as a commercially available bone cement, was purchased to prepare the nano-composite cement samples. The acrylic bone cement is constituted of polymer powder and liquid monomer. The composition of a commercially available bone cement used in this work is listed in Table 1. Moreover, the nano-hydroxyapatite derived from bovine bone (BHA) was selected as bone compatible nano-filler. Weighed amounts of polymer and BHA powders (i.e. 0 wt%, 5 wt%, 10 wt% and 15 wt% of BHA) were mixed with each other using a mixer mill (Retsch MM400, Germany) for 2 min with a vibration frequency of 20 s^{-1}. Vacuum mixing was used to prepare the samples as recommended by other researchers [19,20]. Afterwards, the resulting mixture of polymer and BHA powders with liquid monomer were poured into the vacuum mixing machine and maintained for 15 s under vacuum pressure of 0.7 bars at a temperature of 23 ± 3 °C. The admixture was blended for 30 s and finally held for a further 15 s in the vacuum mixing machine. After mixing the nano-composite components, the mixture dough was injected into each separate cubic mold with dimension of 10 × 10 × 5 mm^3. The nano-composite cement samples were allowed to cure for 15 min in ambient conditions and the samples were subsequently separated from the molds. All samples were grounded with 400–2500 grit sandpapers and after that were polished with an alumina suspension in order to achieve a smooth surface for nano-indentation and nano-scratch tests. The perfect polished samples were kept for two months in the ambient conditions in order to reach to relatively steady state of nano-composite cements before performing nano-indentation and nano-scratch experiments.

2.4. Experiments

The mechanical and tribological properties of the specimens were characterized based on ISO 14577 standard using nano-indentation and nano-scratch test instrument (Triboscope system, Hysitron Inc., USA) equipped with a Berkovich type

Table 1
Composition of commercially available bone cement used in this study.

Powder content (60 g)		Liquid content (30 ml)	
Polymethylmethacrylate	52.56 g	**Methylmethacrylate**	29.64 ml
Benzoyl peroxide	1.44 g	***N,N* Dimethyl p-toluidine**	0.36 ml
Barium sulfate	6.00 g	**Hydroquinone**	18–20 ppm