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ScienceDirect

Ceramics International 41 (2015) 4531–4537

CERAMICS INTERNATIONAL

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Synthesis and fabrication of novel cuttlefish (*Sepia officinalis*) backbone biografts for biomedical applications

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Received 29 October 2014; received in revised form 27 November 2014; accepted 27 November 2014
Available online 5 December 2014

Abstract

New biografts were fabricated via the sol–gel method by using different proportions of cuttlefish (*Sepia officinalis*) backbone and hydroxyapatite powder (HAp). The effect of the different proportions of cuttlefish (CF) on the morphology, mechanical properties and microstructure of the micro and nano scale-HAp were studied. Chemical properties and phase transformations of the fabricated biografts were characterized by SEM, XRD and FTIR analysis. Mechanical properties of the produced grafts were examined by hardness and compression tests. The results showed that crystallinity of the grafts increased with the increasing CF proportions. No significant difference was detected in its strength by changing the particle size of HAp e.g. micro and nano scale-HAp with different proportions of CF backbone. However, porosity and sinterability of the fabricated grafts were noted to increase and cracks on the surface decreased with increasing the CF backbone amount. Also, micro scale-HAp based biografts produced a higher hardness than the nano scale-HAp based biografts. The highest hardness was obtained from the biograft samples containing 40% micro scale-Hap.

Keywords: Bone graft; Hydroxyapatite; Cuttlefish backbone

1. Introduction

Bioceramics are used in diseased and/or defective parts of the hard tissues in the human body [1]. Calcium phosphate containing ceramics are especially known to be a promising materials due to their excellent biocompatibility [2]. Hydroxyapatite (HA) is one of the most conventional bioceramics which are biocompatible and the main component is bone. It has a broad area of use because of its ability to maintain good bonding between bone and its surrounding tissue [3,4]. HAp has an important role in materials chemistry since it has excellent biocompatibility and good chromatographic properties to refine proteins [5,6]. However, the lack of mechanical properties of HAp is probably the only disadvantage of this material [7]. In order to improve its mechanical properties and the biological properties of HAp, a vast number of studies have been conducted over the last 20 years [5,8–11,13]. In this context, as an alternative, Sea-derived natural fish skeletons are also used as calcium phosphate sources due to their structural resemblance to human bone [12–15].

Cuttlefish backbone is a lightweight cellular material and has two main components, the dorsal shield and the lamellar matrix. The dorsal shield is very tough and dense providing a rigid substrate and a lamellar matrix of CF [16,17]. Cuttlefish backbone has been proposed as a suitable raw material for a range of applications. For instance, Poompradub et al. [18] investigated the potential use of cuttlefish backbone as a filler of natural rubber. Even though it was significantly less refined, it was reported that the cuttlefish backbone had comparable mechanical properties to commercially available bone graft fillers. Yildirim et al. [19] investigated a quantitative analysis of mineral substances in raw cuttlefish backbone. They reported that the mineral composition of cuttlefish backbone is similar to human bone tissue but they suggested that the direct use of cuttlefish backbone as a bone tissue scaffold warranted further investigation.

In recent years, the studies on calcium phosphates applications and the usage of these materials in healthcare increased due to its high biocompatibility in the body. Such materials are

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http://dx.doi.org/10.1016/j.ceramint.2014.11.148
0272-8842/

reported to be more suitable for high loading applications [20]. CF backbone is a material which is cost efficient and easy to obtain. Also CF contains porous $CaCO_3$ and Calcium phosphate (Ca–PO_4) structures exhibiting bone like ions. Due to its resemblance to bone structure and because of its composition, crystallinity, pore size and biocompatibility, as it is a natural material, CF backbone can be used as alternative biograft in defected bones [21–23]. Depending on these properties of HAp and CF, micro and nano scale HAp based-CF containing M-H30S20, M-H30S30, M-H30S40 and N-H30S20, N-H30S30, N-H30S40 were synthesized via the sol–gel method and its chemical, morphological and mechanical properties were investigated.

In this study, novel bone grafts were synthesized by the addition of different proportions of CF and sol–gel additives (P_2O_5, Na_2CO_3, KH_2PO_4 and CaO) into both micro and nano scale HA powders. The crystallinity, composition, structures and mechanical properties were characterized by X-ray, FTIR and SEM analysis, respectively. It was shown via SEM images that the grafts have high densification structure and varying hardness and strengths depending up on CF concentration ratios.

2. Experimental

In the present study, nano scale (<200 nm) (Sigma; 1306-06-5) and micro scale (25 μm) HA ($Ca_{10}(PO_4)_6(OH)_2$) (Merck; LR 290280 L41) and micro scale CF were used as main components of the biografts. As for the sintering additive, KH_2PO_4 ($>99.5\%$ purity, Merck-1.04873.0250), Na_2CO_3 ($>99.5\%$ purity, Sigma-497-198), CaO (95% purity, Carlo Erba-331567), P_2O_5 (97.1% purity, Merck-K33152940.418) were used.

CF was provided from Mersin, Turkey (along the coast of the Mediterranean Sea). The CF was washed and dried under vacuum conditions, then mechanically ground in a grinder using alumina balls. The powder particle size was reduced to 14 μm. The obtained CF powder was kept in alcohol for 48 h and then dried in an oven for 28 h at 70 °C. The ground CF powders were homogeneously mixed with HA powder and other additives such as: Na_2CO_3, CaO, P_2O_5 and KH_2PO_4. Then, as shown in Fig. 1, the same proportions of these additives (CaO, KH_2PO_4, Na_2CO_3 P_2O_5) and different proportions of CF (20, 30 and 40%) were added to the micro and nano scale-HA powders and homogeneously mixed using an ultrasonic homogenizer. The obtained gel was then left to dry at 120 °C at normal atmosphere for 24 h. After completely drying, the powders were isostatically compacted and sintered at 1180 °C for 2.5 h in a vacuum. The fabricated grafts were characterized with an X-ray diffractometer, XRD, (BRUKER D8 ADVANCE ($\lambda = 15406$ Å), Fourier transformation infrared spectrometer, FTIR FTIR spectrums were obtained at 4000–400 cm^{-1} range (ALTI Unicam WATTSON 1000) and structural images by scanning electron microscope, SEM (JEOL JSM-7001F). The compression strengths of produced grafts were evaluated with a universal testing machine (Shimadzu, Autograph, 5 kN) at 5 mm/min interval. For the hardness tests, three cylindrical discs for each group (micro-scale HA and nano-scale HA and 20–40% CF doped) specimens having a 10 mm diameter and 1 mm height were prepared. Hardness measurements of the fabricated CF dopped biograft samples were executed on a Future Tech, FM-700 tester with a Vickers pyramid tip under 20 N loading for 5 s time intervals.

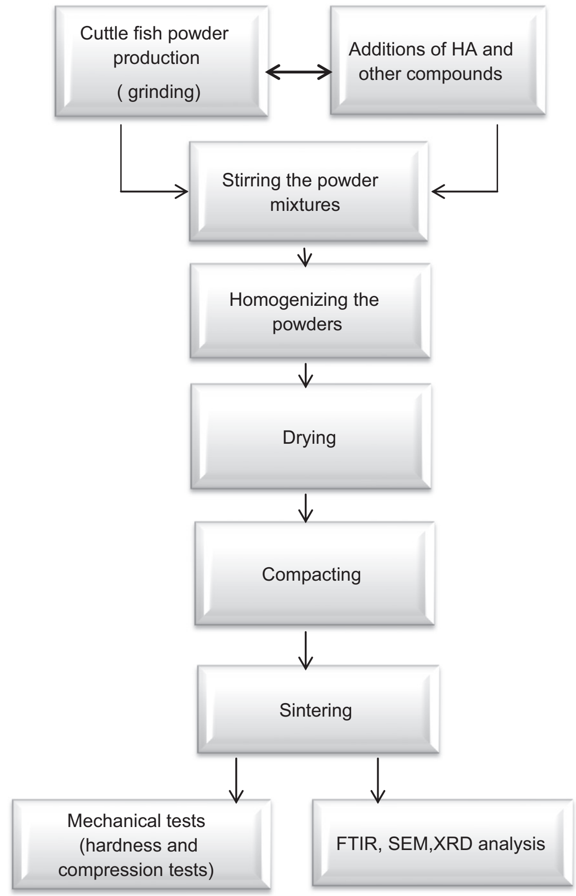

Fig. 1. Experimental flow chart of biograft fabrication process.

3. Results

HAp based CF grafts with ratios between 20 and 40% were synthesized via the sol–gel method. During the synthesis, the additives KH_2PO_4, Na_2CO_3, P_2O_5, CaO were added to increase gelation, densification and sintering properties. The effects of micro and nano scale-HA and different proportions of CF were investigated for 20, 30, and 40% CF additions. Fig. 2a shows the FTIR spectra of the CF containing and micro scale-HA based biografts. The result of using the concentrations (20, 30, 40%) CF ratios and micro scale HAp, a broad and low intensity $(CO_3)^{2-}$ peaks at 2987.53 cm^{-1} was observed. Also at 1167.77–977.32 cm^{-1} intervals and 1023.63 cm^{-1}, a sharp $(PO_4)^{3-}$ peak is seen (Fig. 2a). The results of the biografts produced at 20–30% CF concentration ratios with nano-scale HAp were shown in Fig. 2b. The peak $(PO_4)^{3-}$ is seen at 1086.87–962.78 cm^{-1} intervals. When the micro and nano scale-HA based biografts are compared, the peaks for the nano scale HA based biografts are sharper and narrower. In addition, $(CO_3)^{2-}$ the peak of micro scale HAp based biografts were also observed for nano scale-HA based biografts.

Fig. 3a shows the XRD spectra of the micro scale-HA based, 20, 30, 40% CF concentration rates as M-H30S20, M-H30S30 and M-H30S40 biografts. XRD patterns of nano