Materials Research Bulletin 50 (2014) 432–439

Contents lists available at ScienceDirect

Materials Research Bulletin

journal homepage: www.elsevier.com/locate/matresbu

Fabrication of nano structural biphasic materials from phosphogypsum waste and their in vitro applications

Khaled R. Mohamed [a,*], Sahar M. Mousa [b,c], Gehan T. El Bassyouni [a,d]

[a] Biomaterials Department, National Research Centre, Dokki, Cairo, Egypt
[b] Chemistry Department, Science & Art College, King Abdulaziz University, Rabigh Campus, P.O. Box 344, 21911 Rabigh, Saudi Arabia
[c] Inorganic Chemistry Department, National Research Centre, Dokki, P.O. Box 12622, 11787 Cairo, Egypt
[d] Medical Physics Department, College of Medicine, Taif University, Saudi Arabia

ARTICLE INFO

Article history:
Received 17 March 2013
Received in revised form 3 September 2013
Accepted 5 November 2013
Available online 12 November 2013

Keywords:
A. Composites
A. Nanostructures
C. Electron microscopy
C. X-ray diffraction
C. Infrared spectroscopy

ABSTRACT

In this study, a novel process of preparing biphasic calcium phosphate (BCP) is proposed. Also its bioactivity for the utilization of the prepared BCP as a biomaterial is studied. A mixture of calcium hydroxyapatite (HAP) and tricalcium phosphate (β-TCP) could be obtained by thermal treatment of HAP which was previously prepared from phosphogypsum (PG) waste. The chemical and phase composition, morphology and particle size of prepared samples was characterized by X-ray diffraction (XRD), Infrared spectroscopy (IR), Scanning electron microscopy (SEM) and Transmission electron microscopy (TEM). The bioactivity was investigated by soaking of the calcined samples in simulated body fluid (SBF). Results confirmed that the calcination temperatures played an important role in the formation of calcium phosphate (CP) materials. XRD results indicated that HAP was partially decomposed into β-TCP. The in vitro data confirmed that the calcined HAP forming BCP besides other phases such as pyrophosphate and silica are bioactive materials. Therefore, BCP will be used as good biomaterials for medical applications.

1. Introduction

Phosphogypsum (PG) is an industrial waste generated from phosphoric acid production. Currently, large amounts of phosphogypsum are discarded without any treatment, which lead to considerable land occupation and serious environmental contamination. PG is a by-product composed mainly of gypsum matrix (calcium sulfate dehydrate, $CaSO_4{\cdot}2H_2O$) with other impurities [1,2]. The complete chemical analysis of PG confirmed that the waste was free from radioactive elements and heavy metals such as cadmium (Cd) which is the most pollutant element that could hinder the utilization of the waste [3–5].

PG was converted into HAP [$Ca_{10}(PO_4)_6(OH)_2$], which is one of the most constituents of the biocompatible inorganic materials used in human hard tissues (bone and teeth) [6,7].

There are different kinds of calcium phosphate (CP) bioceramics, with different composition and physical properties. HAP represents the stable phase, with very slow bioresorbability rate. Dense HAP is surface-reactive and can be directly attached to bone through chemical bonding called bioactive fixation [8]. On the contrary, beta tricalcium phosphate (β-TCP) is a bio-resorbable ceramic, on which, natural bone can ingrow after the implantation [9]. The concept of biphasic calcium phosphates (BCP), consisting of intimate mixture of HAP and β-TCP ceramics was developed [10,11]. HAP and β-TCP are commonly used to repair and reconstruct damaged parts of the human skeleton as their Ca/P ratio is close to that of bone (≈1.67) which provide an excellent biocompatibility [12,13]. The degradation rate of β-TCP is 10 times higher than that of HAP, so there are growing interest in developing BCP ceramics due to its controllable degradation rate and more effective bone regeneration ability [14,15]. Also, BCP materials have been reported as a suitable scaffold for hard tissue engineering [16,17].

The contribution of β-TCP is to enhance the degradability; it dissolves faster than HAP in a biological environment followed by the precipitation of carbonated hydroxyapatite (CHA), similar to the biological bone mineral at the implant/tissue interface [18–23]. Pyrophosphate (PP: $Ca_2P_2O_7$) is obvious in the XRD data after heat treatment. PP is one species of the condensed phosphates which are formed through linking tetrahedral [PO_4] units [24]. In bone, calcium pyrophosphate can regulate the onset of calcification and can act as a trigger mechanism to promote mineralization and to alter the rate of crystal growth and dissolution [25–27].

In this study, the industrial waste material (PG) which is cheap and available as by-product was used for preparation of HAP. Different ratios of HAP and β-TCP could be obtained by heat treatment. The powder structures were analyzed using XRD, FT-IR and TEM techniques. The bioactivity assessment was done by

* Corresponding author. Tel.: +20 233371362; fax: +20 233370931.
E-mail address: Kh_rezk966@yahoo.com (K.R. Mohamed).

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http://dx.doi.org/10.1016/j.materresbull.2013.11.023

soaking the calcined samples in simulated body fluid (SBF) and the formed apatite layer was assessed using thin film X-ray (TF), FT-IR and SEM. Also EDX was used for determining the value of Ca/P ratio to confirm the formation of apatite layer on surface of the HAP samples.

2. Experimental

2.1. Materials

The starting materials were the industrial phosphogypsum waste (PG) and phosphoric acid (85%). Ammonia solution (NH_4OH) was used as an agent for adjusting the pH. Distilled water was used during all steps of preparation.

2.2. Method

A simple method was used for the preparation of HAP powder. PG was mixed with distilled water with vigorously stirring at room temperature. The required amount of phosphoric acid was slowly added drop wisely. The pH of the reaction was adjusted to 11 by the addition of ammonia solution. The suitable time to complete the reaction was 1 h [28].

$$5CaSO_4{\cdot}2H_2O + 3H_3PO_4 \rightarrow Ca_5(PO_4)_3OH + 5H_2SO_4 + 9H_2O$$

The resulting product was dried at 80 °C and pressed into tablets of 1.0 cm diameter. The tablets were calcined at three different temperatures 800, 900 and 1000 °C each for 2 h.

2.3. In vitro test

Each liter of SBF was prepared by dissolving of NaCl (7.996 g), $NaHCO_3$ (0.350 g), KCl (0.224 g), $K_2HPO_4{\cdot}3H_2O$ (0.228 g), $MgCl_2{\cdot}6H_2O$ (0.305 g), $CaCl_2$ (0.278 g), Na_2SO_4 (0.071 g) and Tris (hydroxymethyl) aminomethane $C_4H_{11}NO_3$ (6.057 g) using de-ionized water [29]. The pH of the solution was maintained at 7.4 by adjusting amount of 1 M HCl to mimic the concentration of human blood plasma. Also, SBF was fixed at ratio of mass (g)/liquid (ml) in a thermostatic incubator regulated at 37 °C, immersion period was up to 21 days. At the end of each immersion time, the samples were removed, rinsed, dried and analyzed by X-ray, FT-IR and SEM-EDX techniques [30,31].

2.4. Characterization

The structure of PG, HAP and the phases of all the prepared samples before and after calcinations were investigated by X-ray diffraction (XRD), where the diffraction patterns were obtained by using Brukur D8 advanced X-ray diffractometer with Cu-kα radiation. The XRD patterns of the obtained layer of HAP formed on the surface of tablets were recorded by X Pert Pro PANalytical with Cu-kα radiation and secondary monochromator. Infrared measurement (IR) was recorded by (JASCO-FT-IR-3000E) infrared spectrometer in range from 4000 to 400 cm^{-1}. The micrographs of the calcined tablets were investigated by scanning electron microscope (SEM: Jeol-JAX-840A, Japan) with electronic probe microanalyzer. Also, the morphology and particle size were examined by transmission electron microscope (TEM) Jeol JEM 1230, carried out at 100 KeV. The Ca/P ratio was determined by EDX analysis (INCAX-Sight, Oxford instrument, England).

3. Results and discussion

3.1. X-ray analysis

Fig. 1 shows XRD pattern of PG material, where only one phase of pure gypsum $CaSO_4{\cdot}2H_2O$ [JCPDS (06-0047)] was observed. Also

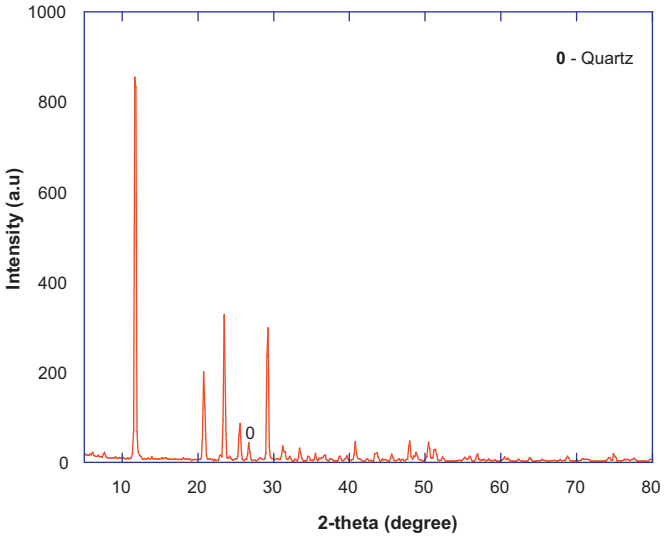

Fig. 1. XRD pattern of PG waste ($CaSO_4{\cdot}2H_2O$).

the characteristic peak of quartz (SiO_2) appeared at d-spacing value 3.34 Å with low intensity [JCPDS (01-0649)]. This result is coinciding with the chemical analysis of PG which has silica in its chemical composition as shown in Table 1. XRD for sample dried at 80 °C shows HAP peaks corresponding to JCPDS (09-432) (Fig. 2) and exhibited broad and weak diffraction peaks which pointed out

Table 1
The chemical analysis of phosphogypsum (PG).

Component	%
Insoluble residue	9.50
H_2O	18.5
CaO	29.25
SO^{-4}	41.5
Fe_2O_3	0.10
MgO	0.20
P_2O_5	0.80
F^- (soluble)	0.10
F^- (insoluble)	0.08
Cd	Not detected

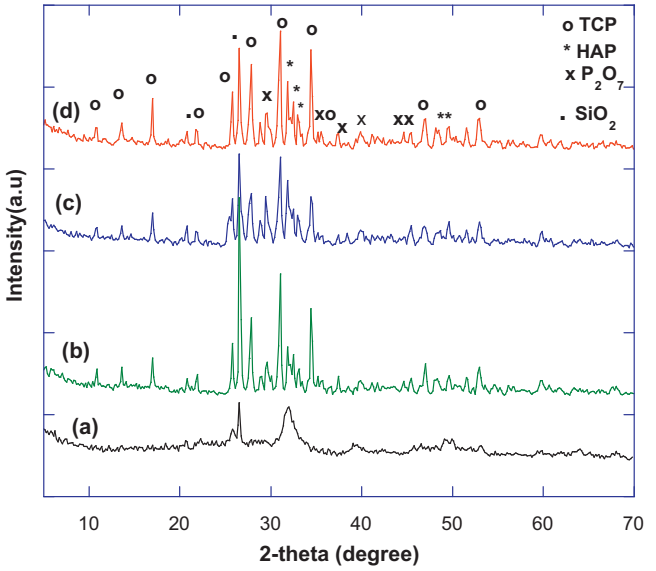

Fig. 2. XRD patterns of HAP dried at 80 °C (a), calcined at 800 °C (b), at 900 °C (c), and at 1000 °C (d).