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In-vitro bioactivity of wollastonite materials derived from limestone and silica sand

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Abstract

This paper describes the behaviour of bioactive wollastonite materials containing Malaysian limestone and silica sand. Wollastonite, which is also known as calcium silicate ($CaSiO_3$), is an industrial mineral composed of calcium, silicon and oxygen. Pseudowollastonite, which is a primary crystal of wollastonite, was synthesised via a solid-state reaction at a temperature of 1450 °C. The in-vitro bioactivity of wollastonite was examined by soaking it in simulated body fluid (SBF) solution for 1–7 days at 36.5 °C. The soaked wollastonite samples were characterised using XRD, SEM-EDX, FTIR and ICP analyses. Apatite particles precipitated on the surface of the wollastonite sample after the sample was soaked in the SBF. The XRD analysis indicated the presence of an increasing amount of the hydroxyapatite phase as the soaking time increased. The SEM and EDX analyses indicated the formation of granules of agglomerated apatite particles on the surface of the soaked wollastonite sample. During the formation of apatite, phosphate ions from the SBF solution were consumed. This process was confirmed by ICP, which revealed a decrease in ion concentration after the soaking process. The FTIR analysis indicated that the peaks of the phosphate ions increase when the apatite layer forms on the surface of the wollastonite sample. After the soaking process, a calcium deficient hydroxyapatite layer was observed on the wollastonite sample. The study concludes that wollastonite produced from Malaysian limestone and silica sand is bioactive and may be used as an implantable biomaterial.

Keywords: Wollastonite; In-vitro bioactivity; Limestone; Silica sand

1. Introduction

Wollastonite, which is also known as $CaSiO_3$, exists in two primary mineral phases, including β-wollastonite (wollastonite) and α-wollastonite (pseudowollastonite) [1,2]. The β-wollastonite mineral is obtained as a natural silicate mineral, whereas α-wollastonite is rarely found in nature [1,2]. The β-wollastonite mineral phase is produced at lower temperatures than is α-wollastonite [2–4], which is apparent in the $CaO–SiO_2$ binary phase diagram, in which the phase transition temperature of β-wollastonite to α-wollastonite is greater than 1125 °C.

Wollastonite is a versatile industrial mineral that is used in ceramics, cements, paints, paper and plastics [4,5]. The versatility of wollastonite has generated much interest due to its promise as a potential implantable material because it can form bonds with bone tissue through the development of a biological apatite layer on the surface [6,7]. Materials with this characteristic are known as bioactive materials and are widely used in medical and dental applications. Many studies have been performed to produce bioactive materials for various applications, such as implantable materials [7–11].

Some calcium silicate materials, such as wollastonite (β-$CaSiO_3$), pseudowollastonite (α-$CaSiO_3$) and dicalcium silicate (Ca_2SiO_4), can bond to bone when in contact with a simulated body fluid (SBF) solution [7,8,12]. Previous studies have also reported that materials containing calcium oxide (CaO) and SiO_2 (silicon dioxide) are bioactive and that the formation of apatite is faster than that of other bioglasses or glass-ceramics in the SBF solution [13,14].

Wollastonite materials have been produced from various sources and exhibit a range of bioactive properties [6–8]. In this paper, the bioactivity of wollastonite synthesised from Malaysian limestone and silica sand via a solid-state reaction is reported. A detailed investigation of the bioactivity of the

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material as a function of different origins of limestone and silica sand has not been fully performed. The aim of this study is to evaluate the formation behaviour of apatite on the wollastonite sample surface after soaking in the SBF solution.

2. Materials and methods

2.1. Preparation of the wollastonite powder

Limestone and silica sand were used as raw materials and collected from Simpang Pulai, Perak and Kota Tinggi, Johor, respectively. The raw materials were ground separately and passed through a 75 μm sieve. The particle size distribution, chemical composition and mineral phase of the raw materials were determined using a particle size analyser (Fritsch Analysette 22), X-ray fluorescence spectroscopy (Shimadzu XRF-1700) and X-ray diffraction (XRD) [Bruker D8 Advanced XRD] [Bruker], respectively. The limestone and silica sand with a molar ratio of 1:1 were mixed and sintered in a box furnace (MODUTEMP) prior to being heated to 1450 °C at a rate of 5 °C min^{-1} for 4 h. The sintered powder was analysed using X-ray diffraction (XRD) [Bruker D8 Advanced XRD] [Bruker] to identify the phase and scanning electron microscopy (SEM) coupled with energy-dispersive X-ray spectroscopy (EDX) [Supra 4P] to study the morphology.

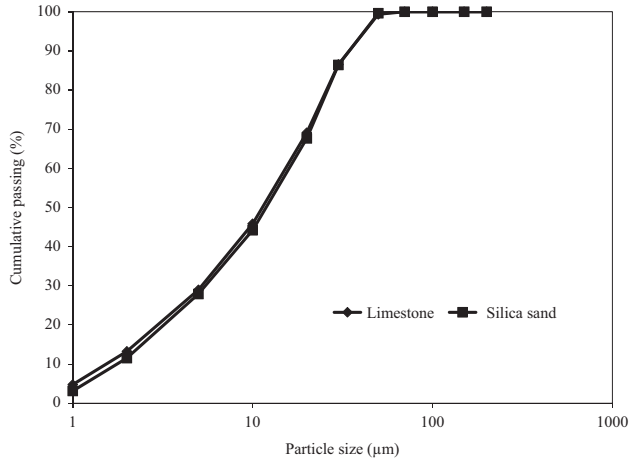

Fig. 1. Particle size distribution of raw materials.

Table 1
Chemical composition of raw materials.

Composition	Limestone (wt%)	Silica sand (wt%)
Na_2O	0.30	–
MgO	0.56	–
Al_2O_3	0.15	0.05
SiO_2	0.20	99.61
CaO	55.41	0.01
K_2O	0.02	–
TiO_2	0.01	0.07
Fe_2O_3	0.05	0.01
LOI	43.30	0.24

2.2. Bioactivity evaluation of wollastonite samples

To examine the bioactivity of wollastonite, 1 g of the powder was pressed with a force of 2.2 T into a disc 13 mm in diameter and 7 mm in thickness. The SBF solution was prepared according to the method described by Kokubo and Takadama [15]. Then, the wollastonite samples were soaked in the SBF solution at a pH of 7.3–7.4 for 1, 3, 5 and 7 days, at a temperature of 36.5 °C. The SBF solution was replaced every 3 days. After the soaking period, the wollastonite samples were washed with acetone, dried and characterised using X-ray diffraction, SEM coupled with EDX and Fourier transform infrared (FTIR) spectroscopy [Bruker Optics]. Ca, Si and P ion concentrations in an unchanged SBF solution were determined using an inductive coupled plasma spectrometer (ICP) [Perkin-Elmer]. The Ca/P ratios for the wollastonite samples were calculated using the atomic % of Ca and P, which was obtained from EDX chemical analysis.

3. Results and discussion

3.1. Characteristics of limestone, silica sand and wollastonite powder

Limestone granules and silica sand were ground for different grinding periods to obtain sized particle that pass through a 75 μm sieve. Limestone had to be ground for 1 h to obtain a mean particle size of 11.57 μm. Silica sand possessed a mean particle size of 12.28 μm after 2 h of grinding. By performing the grinding process separately, a uniform degree of liberation is obtained, which involves a reduction in the particle size and removal of the minerals from limestone and silica sand [16]. Fig. 1 shows the particle size distribution of raw materials. The chemical composition of limestone and silica sand after the grinding process is shown in Table 1.

Fig. 2 shows the XRD patterns of limestone, silica sand and wollastonite powder. The results indicate that Malaysian limestone and silica sand consist of calcite (ICDD 00-005-0586) and quartz (ICDD 00-046-1045), respectively. The sintered mixture of limestone and silica sand was composed of pseudowollastonite

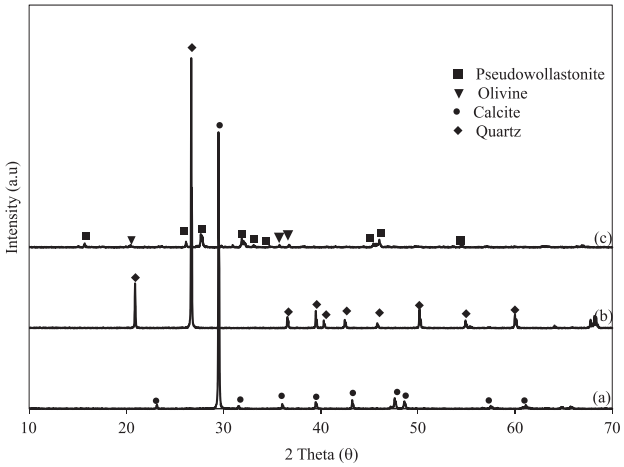

Fig. 2. XRD patterns for (a) limestone, (b) silica sand and (c) synthesised wollastonite.