Journal of Non-Crystalline Solids 426 (2015) 164–168

Contents lists available at ScienceDirect

Journal of Non-Crystalline Solids

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

Modification of dicalcium silicate bone cement biomaterials by using carboxymethyl cellulose

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ARTICLE INFO

Article history:
Received 11 May 2015
Received in revised form 4 July 2015
Accepted 6 July 2015
Available online 16 July 2015

Keywords:
Calcium silicate bone cement;
Carboxymethylcellulose;
Setting time;
Compressive strength;
Bioactivity

ABSTRACT

To ensure the operability of the clinical, the setting time is one of the most clinically vital factors. Sol–gel technique was used to prepare calcium silicate powders with different molar ratios of CaO/SiO_2, and the calcium silicate bone cements (CSCs) were obtained in this study. Functional groups of powder and cements were analyzed by infrared spectroscopy (FT-IR). The doped cement was prepared using carboxymethylcellulose (CMC)-containing calcium silicate powder as solid phase and distilled water as liquid phase. Phase composition, morphology, setting time (St) and compressive strength (Cs) of the doped cement, after mixing with water, were investigated by X-ray diffraction (XRD), scanning electron microscopy (SEM), Gillmore needle and electronic universal material testing machine, respectively. In vitro mineralization of doped cement was investigated by SBF immersion test by soaking the samples individually in 10-ml of simulated body fluid (SBF) solution at 37 °C for 0, 1, 3, 7 and 15 days (d), respectively. The results indicated that the doped cement with 0.10% CMC possessed shorter setting time, higher compressive strength, and desirable bioactivity that makes it an attractive choice for use in vertebroplasty and bone filling surgery.

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1. Introduction

Ceramic materials have been widely used in bone repair, bone filling, artificial bone and so on [1], but it had always been difficult to fabricate the complicated structure of dental applications due to limitations, such as brittleness. The biological bone repair materials, having similar mechanical properties to natural bone, were obtained by combining the bioactive ceramic fine particles and organic polymers. Recently, there has been increasing usage of composite materials in bone replacement and bone filling [2–5]. Studies have shown that $CaO–SiO_2$-based ceramic cement has a good biological activity and can be modified by polymer composite materials [6–8].

To ensure the operability of the clinical, the setting time is one of the most clinically relevant factors. Although a standard setting time was not proposed for root canal filling/sealing of the current clinical procedures, an appropriate and sufficient setting time is essential for a successful surgical treatment [9]. After mixing the water and powders, the injected cement could not maintain shape and support stress during this period due to the long setting duration, which could cause clinical problems [10]. However, the setting time was too short to inject into the defection. Some authors [11,12] indicated that an approximate setting time of 15 min for injectable bone cements was applicable to use in dental treatment, vertebroplasty and keratoplasty.

Sol–gel method was used to prepare calcium silicate powders with different molar ratios of CaO/SiO_2, and CMC was used to modify the calcium silicate bone cements. The setting time, compressive strength and vitro bioactivity were investigated in this study, in addition to other characterizations by XRD, FTIR and SEM. Finally, the hybrid calcium silicate bone cement containing CMC, which can be suitable for clinical application, was prepared in this study.

2. Experimental procedure

2.1. Powder and cement preparation

The powder was prepared by sol–gel method described in a previous work [10]. Reagent-grade tetraethyl orthosilicate ($Si(OC_2H_5)_4$; TEOS, $SiO_2\% \geq 28.4\%$, Sinopharm Chemical Reagent Co., Ltd, China) and calcium nitrate ($Ca(NO_3)_2 \cdot 4H_2O$; 99.0%, XiLong Chemical Co., Ltd, China) were used as precursors for SiO_2 and CaO, respectively. 2 mol/L nitric acid (HNO_3) and absolute ethanol were used as the catalyst and solvent, respectively. The nominal molar ratios of CaO/SiO_2 ranged from 3:7 to 7:3. For simplicity, the sintered powders and the cements derived from such powders were recorded by the same codes throughout this study. As shown in Table 1, for example, the specimen code "C30S70" stands for both sintered powder and cement with $CaO/SiO_2 = 3:7$ (in mol %). The molar ratio of TEOS:($HNO_3 + H_2O$): ethanol was

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http://dx.doi.org/10.1016/j.jnoncrysol.2015.07.014
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Table 1
Composition (molar ratio), setting time (St) and compressive strength (Cs) of calcium silicate bone cements and doped cements.

	Composition	Setting time	Compressive strength
Specimen code	CaO/SiO$_2$	Min	MPa
C30S70	3:7	58.0 ± 0.7	0.94 ± 0.40
C40S60	4:6	37.0 ± 0.8	2.05 ± 0.50
C50S50	5:5	27.0 ± 0.8	15.53 ± 1.80
C60S40	6:4	14.0 ± 0.7	12.02 ± 1.70
C70S30	7:3	11.0 ± 0.9	4.87 ± 0.60
0.05% CMC/C50S50	5:5	18.0 ± 0.8	13.38 ± 1.40
0.10% CMC/C50S50	5:5	15.0 ± 0.7	18.84 ± 2.30
0.20% CMC/C50S50	5:5	13.0 ± 0.9	16.35 ± 1.70

1:10:10 in this study. 2 mol/L HNO_3, absolute ethanol and the required amount of $Ca(NO_3)_2 \cdot 4H_2O$ were added into TEOS solution successively, with 1 h of stirring after each addition. The prepared sol solution was sealed in a teflon beaker and aged at 60 °C for 2 days, following by evaporation of the solvent in an oven at 120 °C for 2 days to obtain dried gel. This gel was then heated in air to 800 °C for 2 h by using a high-temperature furnace and then cooled to room temperature in the furnace to obtain its powder form.

0.05 wt.%, 0.10 wt.%, 0.20 wt.% carboxymethylcellulose (Shandong Everbright Technology Co., Ltd, China) was added into the sintered powder (C50S50) and coded accordingly (i.e. 0.05% CMC/C50S50). The composite powders were then ball-milled for 12 h in ethanol using a centrifugal ball mill (CQ-QM2L, Nanjing Troon New Instrument Co., Ltd, China) and dried in an oven at 60 °C.

For preparing cement, the liquid-to-powder (L/P) ratio of 0.5 ml/g was used for the powders and composite powders. The C50S50 cement without CMC was used as the CSCs control, in regard of adding CMC cements. The mixed cement was poured into a cylindrical stainless steel mold (diameter, 6 mm and high, 12 mm) under a pressure of 0.7 MPa for 1 min using a uniaxial press and incubated at 37 °C and 100% relative humidity, and then allowed to set for 1 day. It is noted that the size (Φ6 mm × 3 mm) of sample was used for soaking test.

2.2. Test and characterizations

Phase analysis of the powder and the cement was carried out using X-ray diffraction (XRD, Geigerflex, Rigaku, Japan) with a monochromated CuKα radiation tube. The surface morphology images were conducted on scanning electron microscope (SEM; S-4800, JEOL, Tokyo, Japan) under an operating current of 20 mA and a voltage of 40 kV. Fourier transform infrared spectroscopy (FT-IR, NEXUS 670, Nicolet, American) was used to analysis the functional groups of samples. According to international standard ISO 9917–1:2007 for water-based cements, a 400-g Gillmore needle with a 1-mm diameter was utilized to measure the setting time of the cement. The final setting time (St) was recorded as the moment when the needle failed to create an indentation of 1 mm in depth in three different areas of the cement cylinder, which were maintained at 37 °C with 100% relative humidity environment. A total of eight specimens were used for testing the St. Compressive strength (Cs) testing was measured on an electronic universal material testing machine (CMT 6203, Shenzhen Shiji Tianyuan Instrument Co., Ltd., Guangdong, China) at a loading rate of 0.5 mm/min. At least 20 specimens were tested for each group. The pH values of SBF solution before and after soaking with the samples for different time point were obtained from the pH meter (PHSJ-3 F, Shanghai Jie Sheng Scientific Instrument Co., Ltd.). The determined values were calculated using mean ± standard deviation.

2.3. In vitro bioactivity test

Each 24 h set cylindrical specimen (Φ6 mm × 3 mm) was soaked in SBF solution according to the procedure described by Kokubo et al. [13], for predetermined periods of time at 37 °C to evaluate the in vitro bioactivity. After immersing at each time point (0, 1, 3, 7, 15 days), specimens were removed from the centrifuge tube and gently rinsed three times with deionized water and acetone, and then dried at room temperature for XRD, FT-IR and SEM analyses.

3. Results and discussions

3.1. Phase composition and FT-IR spectra of powders

Fig. 1a shows the x-ray diffraction analysis of the five CaO–SiO$_2$ powders sintered at 800 °C for 2 h, indicating that the phase evolution is dictated by the Ca–Si ratios of the precursors. The XRD exhibits a distinct and diffuse diffraction peak at around $2\theta = 32°–34°$, which can be attributed to the β-dicalcium silicate (β-Ca_2SiO_4, JCPDS 29-0371) phase. The result suggests that the more content of CaO in precursors, the stronger of the peak intensities of β-Ca_2SiO_4 and CaO ($2\theta = 37.5°$). It shows that calcium as a promoter played a very important role in the CaO–SiO$_2$ system, additionally, the amount of CaO in the starting materials may affect St [14].

Fig. 1b indicates that the trends in the FT-IR spectra of the prepared powders were similar to those in XRD. For the sample with lowest content of CaO (C30S70), the IR absorption band was assignable to SiO_4 asymmetric stretching extends, ranging over a wide wave number from 1300 to 900 cm^{-1}. The bands at 1550 and 1380 cm^{-1} were ascribed to the vibration of CO_3 groups carbonized from the atmosphere. The band at around 550–530 cm^{-1} originated from the vibration of the siloxane backbone [15]. When the CaO content was equal to the SiO$_2$ content (C50S50), a broadening and shifting to lower frequency in Si–O–Si asymmetric stretching bands were detected in the FTIR spectra, which indicated that the specimens' structure became

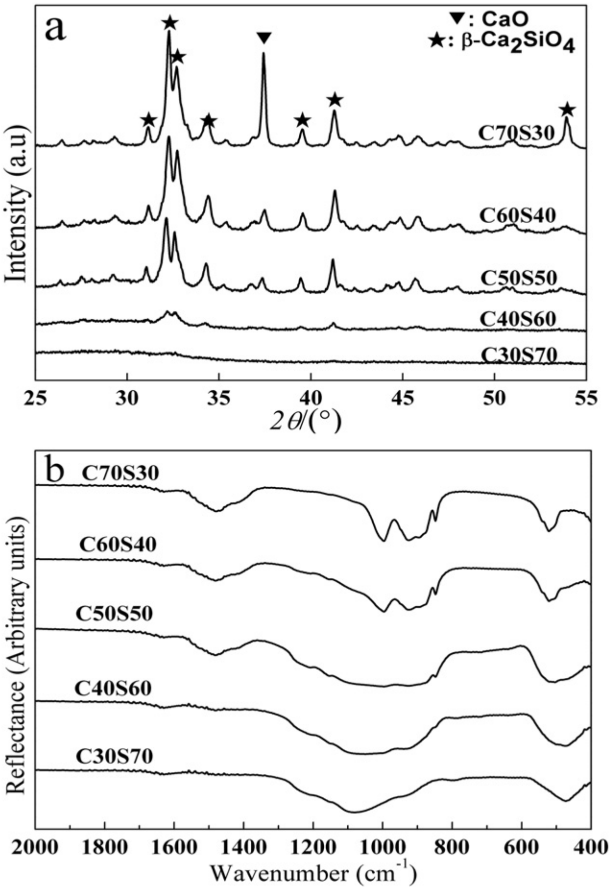

Fig. 1. XRD (a) and FT-IR (b) patterns of calcium silicate powders sintered at 800 °C.

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