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Interphase coordination design in carbamate-siloxane/vaterite composite microparticles towards tuning ion-releasing properties

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ABSTRACT

Siloxane-containing vaterite (SiV) microparticles were prepared with controlling the degree of aminopropyl-functionalization in the siloxane; they are aiming for applications as bone regenerative devices. The aim of this work was to evaluate the structure at siloxane/vaterite interphase and to control the solubility of particles by the structural tuning of siloxane. The particles were spherical with average diameters of 1.1–1.4 μm. Differential infrared spectrometry revealed the transformation of aminopropyl terminals in the siloxane into carbamate (NH-COO⁻) groups. Moreover, the vaterite crystallites in the particles were slightly oriented towards the (001) plane. These results describe the interphase structure, with the carbamate groups coordinating on the Ca²⁺ ion face in the (001) plane of neighbouring vaterite. Upon soaking in buffer solution, the particles exhibited a rapid initial release of Ca²⁺ ions within 30 min and of soluble silica within 2 h. The vaterite in this particle survived for more than 6 h. The chemical stability of the siloxane was enhanced by incorporating tetraethoxysilane-derived siloxane with fractions of 24 mol% or 50 mol%. This enhancement controlled the initial release of not only soluble silica but also Ca²⁺ ions.

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1. Introduction

Process of bone formation is regulated by the transaction of growth factors (GFs) among the cells [1,2]. After the report published by Hench et al., an inorganic product made from Bioglass[®] 45S5, which dominantly contains soluble silica and Ca²⁺ ions, has been reported to genetically stimulate osteoblast cells by enhancing GFs expression [3–6]. Osteogenic promoters made of inorganic components have reliability in incorporation into various biomaterials for bone-reconstruction surgery and are expected to possess a long shelf-life because of their chemical stability against GFs.

The authors previously developed a method for the preparation of siloxane-containing vaterite (SiV) particles using a carbonation process [7–12]. Vaterite is a polymorph of calcium carbonates with a minimum thermodynamical stability. In SiV, vaterite with 5–20-nm-sized lamellae are present, which are enclosed by aminopropyl triethoxysilane(APTES)-derived siloxane (Ap-S) [9]. When the SiV particles are soaked in a physiological pH buffer solution, the

Si–O–Si bond in the Ap-S hydrolyses to release soluble silica, following the subsequent release of Ca²⁺ ions from the dissolution of vaterite. SiV particles were incorporated into poly(lactic acid) (PLA)-based electrospun fiber mats [7,8,12]. When implanting at a defect in rabbit calvaria, bone nodules formation was confirmed in the middle part of the fiber mat after 4 weeks [8].

The stimulant activities of the soluble silica and Ca²⁺ ions have been reported to be dose-dependent. Hench et al. reported that enhanced IGF-II expression in human adult osteoblasts was observed at the concentrations of Si from soluble silica and Ca²⁺ ion ([Si] and [Ca]) of 16.58 and 88.35 μg/ml (~0.6 and 2.2 mmol L⁻¹), respectively [3]. Tsigkou et al. reported that cell culture media supplemented with soluble silica by the [Si] of 15 and 20 μg/ml (~0.5 and 0.7 mmol L⁻¹) supported the enhanced proliferation and differentiation of foetal osteoblasts [13,14]. For the Ca²⁺ ions, the local elevation of the ion concentration in extracellular fluid ([Ca²⁺]_o) to levels as high as 40 mmol L⁻¹ is known to enhance the mitosis of osteoblasts [15–17]. The proliferation, differentiation, and mineralisation of murine osteoblasts were individually enhanced at specific levels of [Ca²⁺]_o [18–20]. Therefore, the adjustment of the ion concentrations and their releasing

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span towards specific levels is desired to achieve effective stimulation in the osteoblast cells.

We previously demonstrated a simple method for reducing the releasing amount of Ca^{2+} ions from SiV by enhancing the degree of (001)-preferred crystal orientation in vaterite crystals [11]. The (001) plane of vaterite possess a high surface energy as the plane composed of Ca^{2+} or CO_3^{2-} ion. Preparation of vaterite with (001)-preferred crystal orientation has been reported in the presence of macromolecules which stabilize the plane [21–25]. The mechanism for the crystal orientation in the presence of Ap-S, however, remained unclear. To the best of our knowledge, the interaction between Ap-S and vaterite has not yet been discussed in any reports.

Herein, the structures of SiV particles containing Ap-S with 0–100 mol% of total siloxane were compared to understand the role of the amino terminals in the Ap-S interphase structure between the vaterite crystals and siloxane. Moreover, the dissolution behaviours of the particles in a physiological pH buffer solution were characterised; this brings a point of view for controlling structures towards tuning the dissolution behaviours of the SiV particles.

2. Experimental section

2.1. Synthesis and characterisation of SiV particles

The SiV particles were prepared by a carbonation process. Briefly, 25 ml of distilled water and 37.5 g of calcium hydroxide (Yabashi Industries Company, Ltd., Japan) were added to 500 ml of methanol (Wako Pure Chemicals Inc., Japan, Medical grade) while stirring. Then, 60 ml of APTES (Sigma-Aldrich, USA, reagent grade, $4.48 \times 10^{-3} \text{ mol cm}^{-3}$), tetraethylorthosilicate (TEOS) (Sigma-Aldrich, USA, reagent grade, $4.48 \times 10^{-3} \text{ mol cm}^{-3}$), or their mixture was added to the slurry. Each reagent was added at 20-min intervals. Carbon dioxide gas (industrial grade, 99.5%) was introduced to the slurry at a rate of 2 L min^{-1} for 60 min. The resulting slurry was aged for 12 h at room temperature and then heated at 110°C for 24 h to remove residual solvents. The resulting powder was dissociated with an agate mortar and pestle to form SiV particles. Hereafter, the samples are called $\text{SiV}_{x\text{AyT}}$, where x and y represent the volume percent (almost similar to mole percent) of APTES and TEOS in total silane, respectively. The sample codes and recipes of the SiVs are summarised in Table 1.

The silicon and calcium contents of the SiV particles were estimated using X-ray fluorescence spectrometry (Hitachi High-Tech Science Corporation, SEA-2210A:XRF, $n = 5$). Vaterite particles with no silane addition were also prepared using the carbonation process. X-ray diffractometry (PANalytical, X'Pert-MPD: XRD) and attenuated total reflectance Fourier-transform infrared spectrometry (JASCO, FTIR 4000 spectrometer equipped with an ATR PRO 450-S attachment: ATR-FTIR) techniques were used to examine the crystal and chemical structures of the particles. ^{29}Si magic-angle spinning nuclear magnetic resonance spectrometry (^{29}Si MAS-NMR; Varian, UNITY Inova 400 plus NMR spectrometer, operated at 79.49 MHz) was used to examine the chemical structure of the siloxane. The morphologies of the particles were examined by

scanning electron microscopy (SEM) using an accelerating voltage of 15 kV (JEOL, JSM-6301F). The mean diameters of the particles were estimated from the SEM images using ImageJ software (<http://rsbweb.nih.gov/ij/>, $n = 50$).

2.2. Dissolution of SiV particles

Tris buffer solution (TBS) was prepared by dissolving 6.118 g of tris(hydroxymethyl)aminomethane into 900 ml of distilled water at 36.5°C . The pH was adjusted to 7.40 using 1.0 mol L^{-1} hydrochloric acid solution. The resulting solution was transferred to a 1000-ml volumetric flask and brought to the volume with distilled water to obtain 0.05 mol L^{-1} TBS. In polystyrene containers, 0.5 g of SiV particles were immersed in 25 ml of the TBS and incubated at 36.5°C . After 0.5–24 h of soaking, the samples were filtered and then dried at 50°C . The dried samples were evaluated by XRD and ATR-FTIR. The [Si] and [Ca] in the soaking solutions were measured using inductively coupled plasma atomic emission spectrometry (Shimadzu, ICPS-7000: ICP-AES) ($n = 3$).

3. Results and discussion

3.1. Characteristics of vaterite microparticles containing APTES- and TEOS-derived siloxanes

Fig. 1 presents SEM images of the SiV particles. Their mean particle sizes and silicon and calcium contents are summarised in Table 2. The particles exhibited slightly compressed spherical morphologies. $\text{SiV}_{100\text{A}}$ had the largest mean diameter, i.e., $\sim 1.4 \mu\text{m}$, among them. The others exhibited the mean diameters of $\sim 1.1 \mu\text{m}$. All of these particles exhibited narrow size distributions. According to XRF analysis, $\text{SiV}_{100\text{A}}$, $\text{SiV}_{70\text{A}30\text{T}}$, and $\text{SiV}_{50\text{A}50\text{T}}$ contained $\sim 2.5 \text{ wt}\%$ silicon, which was greater than that of $\text{SiV}_{100\text{T}}$, namely 1.3 wt%. The Si/Ca mass ratio of $\text{SiV}_{100\text{T}}$ was estimated to be 0.03, which was only one-third of the raw materials composition (Tables 1 and 2). The ratio in the other SiV particles exhibited minor decreases from the value in their precursor slurries. These results suggested that APTES played a key role in the incorporation of siloxane into vaterite.

Fig. 2 presents the ^{29}Si MAS-NMR spectra of the SiV particles. In the $\text{SiV}_{100\text{A}}$ spectrum, the peaks of the trivalent silicon (T^n) species (T^1 : -48 ppm , T^2 : -59 ppm , T^3 : -68 ppm) attributed to the Ap-S are observed. The peaks of tetravalent silicon (Q^n) species (Q^2 : -94 ppm , Q^3 : -101 ppm , Q^4 : -111 ppm) originating from the TEOS-derived siloxane (Te-S) are observed in the $\text{SiV}_{100\text{T}}$ spectrum. Both T^n and Q^n peaks are observed in the spectra of $\text{SiV}_{70\text{A}30\text{T}}$ and $\text{SiV}_{50\text{A}50\text{T}}$; these SiV particles contained siloxane consisting of both APTES and TEOS. The $T^n:Q^n$ molar ratios were estimated to be 76:24 and 50:50 for $\text{SiV}_{70\text{A}30\text{T}}$ and $\text{SiV}_{50\text{A}50\text{T}}$, respectively, as shown in Table 3. These ratios nearly followed the APTES:TEOS composition ratios in their raw materials. The relations between these structures and the dissolution profiles of SiV particles will be discussed later.

Fig. 3 presents the ATR-FTIR spectra of the SiV particles. The spectrum of vaterite is also shown as a reference. Absorption bands

Table 1
Nominal compositions for preparing various SiV particles.

Sample	APTES		TEOS		$\text{Ca}(\text{OH})_2$ [g]	Si/Ca (mass ratio)
	Vol. [ml]	Mass [g]	Vol. [ml]	Mass [g]		
$\text{SiV}_{100\text{A}}$	15.0	1.80	–	–	37.5	0.09
$\text{SiV}_{70\text{A}30\text{T}}$	10.5	1.26	4.5	0.57		0.09
$\text{SiV}_{50\text{A}50\text{T}}$	7.5	0.90	7.5	0.94		0.09
$\text{SiV}_{100\text{T}}$	–	–	15.0	1.89		0.09

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