



Fabrication of calcite blocks from gypsum blocks by compositional transformation based on dissolution–precipitation reactions in sodium carbonate solution

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ABSTRACT

Calcium carbonate (CaCO_3) has been used as a bone substitute, and is a precursor for carbonate apatite, which is also a promising bone substitute. However, limited studies have been reported on the fabrication of artificial calcite blocks. In the present study, cylindrical calcite blocks ($\phi 6 \times 3$ mm) were fabricated by compositional transformation based on dissolution–precipitation reactions using different calcium sulfate blocks as a precursor. In the dissolution–precipitation reactions, both $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ and CaSO_4 transformed into calcite, a polymorph of CaCO_3 , while maintaining their macroscopic structure when immersed in 1 mol/L Na_2CO_3 solution at 80 °C for 1 week. The diametral tensile strengths of the calcite blocks formed using $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ and CaSO_4 were 1.0 ± 0.3 and 2.3 ± 0.7 MPa, respectively. The fabrication of calcite blocks using $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ and CaSO_4 proposed in this investigation may be a useful method to produce calcite blocks because of the self-setting ability and high temperature stability of gypsum precursors.

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1. Introduction

The inorganic component of vertebrates' skeletons is apatite, whereas invertebrates employ calcium carbonate (CaCO_3) as the inorganic component of their exoskeleton. Although both apatite and CaCO_3 are known to show excellent tissue response and good osteoconductivity, few studies investigating artificial CaCO_3 as an artificial bone substitute have been conducted.

CaCO_3 has three polymorphs, which are calcite, aragonite, and vaterite. Calcite is the most thermodynamically stable polymorph of CaCO_3 , followed by aragonite and then vaterite. CaCO_3 blocks are found in nature and have also been fabricated artificially. Regarding the use of natural CaCO_3 blocks as a bone substitute, Walker reported in 1983 that calcite bonded to bone [1]. Fujita implanted calcite plates taken from limestone in rabbit tibia and also found that bone bonded to calcite [2]. The use of natural vaterite as a bone substitute has not been reported. This may be because vaterite is very rare in nature. In contrast to calcite and vaterite, many studies on aragonite have been reported. Marine coral is composed of aragonite, and has been studied extensively and used in clinics (Biocoral™, Biocoral Inc.) because of its

excellent tissue response and interconnected porous structure. Guillman et al. [3] implanted marine coral in dogs and found that coral was resorbed and replaced with new tissue. They attributed the resorption of marine coral to enzymatic attack, especially by carboanhydrase. Osteoconductivity and replacement of marine coral with bone have been reported in numerous papers [4–11]. Marine coral can be used not only as a bone substitute but also as a precursor in the fabrication of hydroxyapatite [HAp; $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$] blocks, which are also a bone substitute. Roy and Linnehan reported that HAp formed when marine coral skeleton was immersed in ammonium phosphate solution under hydrothermal conditions because of a hydrothermal exchange reaction between carbonate and phosphate [12]. Coralline apatite (Pro Osteon®, Interpore Cross) prepared by this route has been used in clinics with good results [13–18].

In contrast to the studies and clinical use of natural CaCO_3 blocks as a bone substitute, artificial CaCO_3 blocks have seldom been investigated as a bone substitute. To date, only calcite blocks have been used an artificial CaCO_3 block bone substitute [24]. One of the methods used to fabricate calcite blocks is to expose a calcium hydroxide [$\text{Ca}(\text{OH})_2$] compact to CO_2 under high humidity at relatively low temperature [19–22]. In this carbonation reaction, high humidity is needed for the carbonation of the $\text{Ca}(\text{OH})_2$ compact because this process is based on a dissolution–precipitation reaction as follows. Ca^{2+} dissolved from $\text{Ca}(\text{OH})_2$

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[Eq. (1)] and CO_3^{2-} formed by the dissolution of CO_2 in H_2O [Eq. (2)] react with each other and precipitate as calcite crystals [Eq. (3)]. The precipitated calcite crystals interlock with each other to produce a calcite block [22].



Alternatively, calcite blocks can be fabricated by exposing a Ca(OH)_2 compact to CO_2 at higher temperature by direct carbonation of Ca(OH)_2 [23,24], as summarized in Eq. (4).



Using the direct carbonation process in Eq. (4), a porous calcite block was obtained by exposing a Ca(OH)_2 compact containing chopped nylon fiber at 770 °C to 50% CO_2 –50% O_2 . Sintering at 800 °C resulted in the formation of CaO , which tends to slake, while sintering at 750 °C resulted in incomplete burn out of the nylon fiber [24]. The porous calcite block exhibited good tissue response and bone bonding ability, leading to the bone penetrating into the interior of the block macropores [24].

Artificially fabricated calcite blocks have been found to transfer their composition to apatite, similar to the behavior of natural aragonite [25–32]. Interestingly, transformation of artificially fabricated calcite blocks to apatite ones did not require hydrothermal conditions, occurring at as low as 60 °C by simply immersing the calcite blocks in sodium phosphate solution. Also, artificially fabricated calcite transformed into not HAp but carbonate apatite [CO_3Ap ; $\text{Ca}_{10-a}(\text{CO}_3)_b(\text{PO}_4)_6-c(\text{OH})_2-d$] [25–32].

Although the polymorph of marine coral is aragonite and that of artificial CaCO_3 fabricated by exposing Ca(OH)_2 to CO_2 is calcite, the different polymorphs cannot be the reason for the different temperatures required for the compositional transformation reaction because aragonite is more reactive than calcite. Therefore, the main reason for the different temperatures required for the compositional transformation reactions of marine coral and artificially fabricated calcite blocks is thought to be the presence of impurities in marine coral. Marine coral contains both organic and inorganic impurities, and both are believed to prevent its compositional transformation. The organic components coat the aragonite crystals, blocking the reaction of aragonite with the phosphate salt solution. These organic components would not dissolve in the aqueous solution at low temperature but would dissolve at the high temperatures used in hydrothermal treatment. Inorganic impurities such as magnesium and fluorine also limit the reaction of aragonite crystals with the phosphate salt solution. However, under hydrothermal conditions, aragonite reacts with the ammonium phosphate solution because the inhibitory effect of magnesium and fluorine is weaker at higher temperature.

Obviously, artificial porous bone substitutes fabricated using only pure chemicals are desired. As stated above, porous calcite blocks can be fabricated using Ca(OH)_2 compacts containing chopped nylon fibers as a porogen. However, the temperature range that allows the nylon fibers to be burned out without forming CaO is very limited. Also, a larger amount of chopped nylon cannot be introduced because the elasticity of the nylon fibers causes compacts with higher fiber contents to lose their shape [29].

Compared with Ca(OH)_2 , calcium sulfate (gypsum) is more stable at high temperature. This means that a polymer porogen can be easily burned out without causing the thermal decomposition of calcium sulfate. In addition, calcium sulfate has self-setting ability, so a larger amount of nylon fibers can be introduced into the calcium sulfate blocks compared with that in Ca(OH)_2 compacts. Also, any structure can be

made from calcium sulfate using a three-dimensional printing system [33,34].

If a calcium sulfate block can transform into a CaCO_3 block while maintaining its macroscopic structure, fabrication of CaCO_3 blocks with a desired structure will become possible. In turn, this will allow fabrication of CO_3Ap blocks with desired structure. Therefore, the objective of this study is to evaluate the feasibility of fabricating calcium carbonate blocks from calcium sulfate ones based on dissolution–precipitation reactions while maintaining the macroscopic structure of the precursor block by simply immersing a calcium sulfate block in sodium carbonate solution.

2. Materials and methods

2.1. Fabrication of calcium sulfate blocks and their compositional transformation

Calcium sulfate hemihydrate ($\text{CaSO}_4 \cdot 0.5\text{H}_2\text{O}$, New Fuji Rock White, GC, Tokyo, Japan) was mixed with water with a mixing ratio of water to powder of 0.2. The resulting paste was poured into a plastic mold and left for 1 h to give set gypsum or calcium sulfate dihydrate ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) samples with a diameter of 6 mm and thickness of 3 mm. The set gypsum blocks were heated to 800 °C at a rate of 5 °C/min and then kept for 5 h at 800 °C to form anhydrous calcium sulfate (CaSO_4) blocks.

Disk-shaped $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ blocks before and after heat treatment were immersed in 1 mol/L Na_2CO_3 (Nacalai Tesque, Kyoto, Japan) at 50 or 80 °C for a prescribed period of up to 3 weeks. The period of immersion in Na_2CO_3 solution of each sample is stated in parentheses. For example, CaSO_4 immersed in Na_2CO_3 solution for 7 days is denoted as CaSO_4 (7 d).

2.2. Compositional analysis

The composition of the disk-shaped samples was evaluated by powder X-ray diffraction (XRD) analysis. The samples were ground to fine powders and then XRD patterns were recorded using a diffractometer (D8 Advance, Bruker AXS GmbH, Karlsruhe, Germany) using $\text{CuK}\alpha$ radiation generated at 40 kV and 40 mA. Samples were scanned from 2θ of 10° to 40° (where θ is the Bragg angle) in a continuous mode.

Quantitative analysis was performed based on the obtained XRD patterns. A calibration curve for the quantitative analysis of CaCO_3 was constructed using a mixture of $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ ($2\theta = 11.78^\circ$) and CaCO_3 ($2\theta = 29.54^\circ$), or a mixture of CaSO_4 ($2\theta = 25.60^\circ$) and CaCO_3 ($2\theta = 29.54^\circ$). The compositional ratio (%) of each CaCO_3 block transformed from the starting $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ or CaSO_4 block was calculated from the integrated area ratio of each XRD pattern using EVA15 software (Bruker AXS GmbH).

2.3. Physical properties

Fractured surface morphology of samples was observed by a scanning electron microscope (SEM, S3400 N, Hitachi High Technologies, Co. Ltd., Tokyo, Japan) at an accelerating voltage of 15 kV after gold–palladium coating by magnetron sputtering (MSP-1S, Vacuum Device Co., Ibaraki, Japan).

Mechanical strength of the disk-shaped samples was evaluated in terms of their diametral tensile strength (DTS). After drying the samples at 60 °C for 24 h, their diameter and thickness were measured using a micrometer (MDC-25MU, Mitutoyo Co. Ltd., Kanagawa, Japan) and the samples were weighed using a microbalance. Then, the samples were crushed with a universal testing machine (AGS-J, Shimadzu, Kyoto, Japan) at a constant crosshead speed of 10 mm/min. The mean DTS value for eight samples was calculated and is expressed as mean \pm standard deviation (SD).

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