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Development of macropores in calcium carbonate body using novel carbonation method of calcium hydroxide/sodium chloride composite

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Abstract Calcium carbonate is one of the bioceramics and has been used clinically as a bone substitute in dental and orthopedic surgery. Introduction of macropores into the bioceramics is highly recommended because those pores enable tissue ingrowth and accelerated osteointegration. We tried to prepare calcium carbonate body with macropores through the new carbonation method of calcium hydroxide/sodium chloride composite. Sodium chloride acted as a water-soluble porogen in developing macropores in calcium carbonate body and was removed completely by washing with distilled water after carbonation. We investigated effects of sodium chloride content and molding pressure on the porosity and the mechanical strength of the calcium carbonate body. Through this study, it was found that the porosity of body increased with the sodium chloride content in composite and was hardly affected by molding pressure. On the other hand, the mechanical strength was increased with the molding pressure and reduced with the porosity. In addition, the increase in content of sodium chloride caused the enlargement of hole size as well as the enhancement of extent of interconnection among pores through hole. Especially, the calcium carbonate body with over 90% porosity could be prepared when 90 wt.% sodium chloride was used under 10 MPa molding pressure. Its average pore and hole size were 177 and 80 μm, respectively.

Introduction

Bioceramics in biomaterial fields have been developed to replace osseous tissues and complete autografts and allografts. Many researches with respect to them have been placed on the fabrication of bioceramics with porous configuration [1–5].

Calcium carbonate ($CaCO_3$), which is biocompatible and biodegradable, can be used not only as a bioceramic itself but as a precursor of carbonate apatite which is analogous to the inorganic component of vertebrate's hard tissue [3, 6–8]. Although several methods for the preparation of $CaCO_3$ have been reported, they are mostly concerned with the fabrication of its powder [9–12]. Even if it has been fabricated in the form of cylinder or other shape, there have been very a few active efforts to develop appropriate pore or to enhance porosity until now [3, 13].

The pore size and porosity of bioceramics play an important role in tissue ingrowth with an internal surface area available for cell adhesion, spreading and expansion, adsorption of biologic metabolites, and resorbability at controlled rates to match that of tissue repair [14]. It is generally accepted that if the pore size is in the range of 100–400 μm, this macropore allows bone tissue ingrowth, making direct integration with bone to improve the mechanical fixation of the implant at the implantation site and nutrient delivery to the center of the regenerated tissue [15–17]. When an implanted macroporous bioceramic is progressively replaced by natural bone, its biomechanical properties resemble more and more those of natural bone [15].

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The impregnation and gel-casting of foams, the inclusion of porogenic volatile or soluble substances, and the dual phase mixing have been proposed for the development of macropores in bioceramics [3, 18–21]. However, a high temperature treatment employed by the most of these methods is not suitable for the fabrication of macroporous $CaCO_3$ body because it decomposes into calcium oxide (CaO) and carbon dioxide (CO_2) at high temperature [22]. In our previous work [23], we have already introduced the novel method of fabrication of pure $CaCO_3$ block using the carbonation of calcium hydroxide block at room temperature. Moreover, the low temperature processing enables addition of different kinds of proteins, antibiotics, antiinflamatory, anticancer drugs, etc into the material [24–27].

The present study reports the method of preparation of macroporous calcium carbonate body using sodium chloride as a porogen by previously reported carbonation method. In order to impart mechanical strength to macroporous calcium carbonate body we applied molding pressure while preparing calcium hydroxide/sodium chloride composite. The change of NaCl content and molding pressure were chosen as experimental parameters and experiments were designed to achieve: increase in the porosity under a low molding pressure, enhancement of the mechanical strength under constant sodium chloride content and increase in the porosity of the body under high molding pressure. It was investigated how degree of carbonation, pore and hole size formed in pores, porosity, and mechanical strength of body are affected by the experimental parameters.

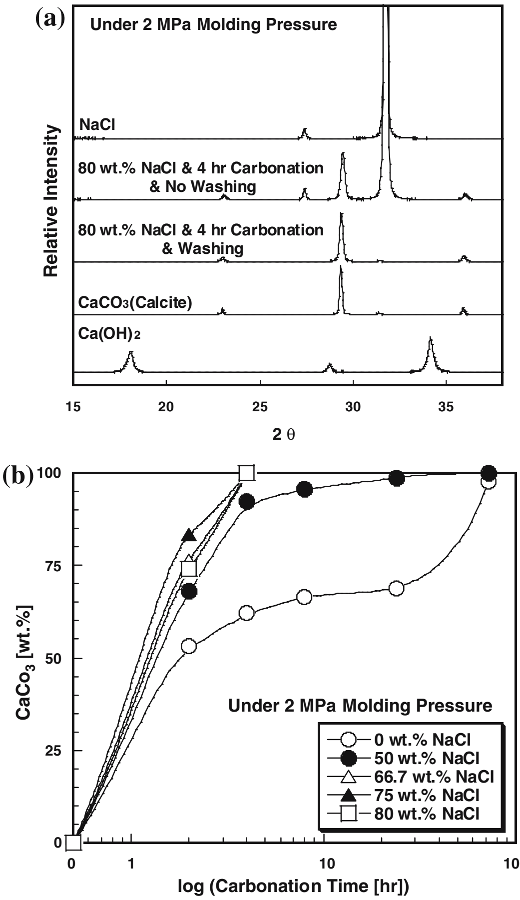

Fig. 1 (**a**) Powder XRD patterns of the $Ca(OH)_2$/NaCl composite containing 80 wt.% NaCl prepared at 2 MPa molding pressure after 4 h carbonation. (**b**) Changes of $CaCO_3$ content in the $Ca(OH)_2$/NaCl composites with carbonation time at various NaCl content under 2 MPa molding pressure

Materials and methods

Preparation of calcium hydroxide/sodium chloride composite

Calcium hydroxide ($Ca(OH)_2$; Wako Chemicals, Osaka, Japan) and sodium chloride (NaCl; Wako Chemicals, Osaka, Japan) were used for the present study. The particle size distribution of $Ca(OH)_2$ with irregular shape was from submicron to several micron. NaCl was pulverized mechanically and sieved to obtain 106–300 μm particulates before used. A variety of mixtures were prepared manually using 0.2 g $Ca(OH)_2$ and NaCl in the 0–90 wt.% range. Each mixture was subject to pressure uniaxially in stainless steel die of 10 mm in inner diameter using an oil pressure press machine (Riken Power, Riken Seiki, Japan) at the molding pressure of 2–10 MPa to prepare $Ca(OH)_2$/NaCl composite.

Carbonation and washing of $Ca(OH)_2$/NaCl composite

The composites were carbonated in carbon dioxide reaction vessel for 2–72 h at room temperature. The reaction vessel, approximately 5 l, was saturated with water vapor and carbon dioxide gas was supplied at a rate of 0.15–0.2 l/min. Subsequently, the composites carbonated were washed sufficiently with distilled water at 60 °C for 24 h to drive off NaCl completely and dried at 60 °C for 24 h.

Characterization

Mechanical testing

The mechanical strengths of composites after carbonation and washing were evaluated in terms of diametral tensile strength (DTS) at room temperature at a constant crosshead rate of 1 mm min^{-1} on an universal testing machine

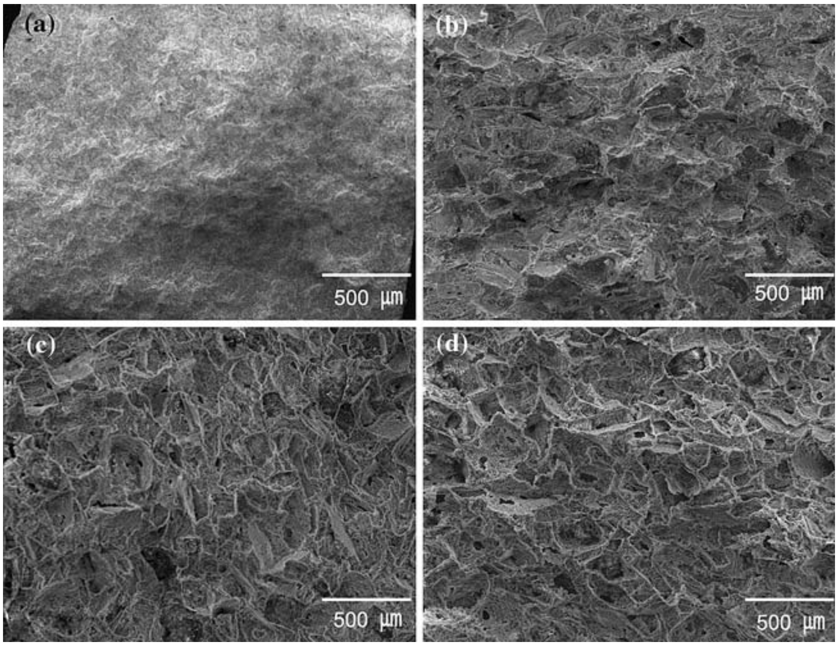

Fig. 2 Scanning electron microscopic observation of the fracture surfaces of $CaCO_3$ bodies under 2 MPa molding pressure. (**a**) 0 wt.% NaCl & 72 h carbonation (**b**) 66.7 wt.% NaCl & 8 h carbonation (**c**) 75 wt.% NaCl & 8 h carbonation (**d**) 80 wt.% NaCl & 8 h carbonation

(SV–301, IMADA, Toyohashi, Aichi, Japan). Five samples were tested for each experimental condition.

X-ray diffraction analysis

The composites after carbonation or carbonation and washing were ground into fine powders. X-ray diffraction (XRD) analysis was carried out using these powders. The XRD patterns were recorded with vertically mounted diffractometer system (RINT 2500 V, Rigaku, Tokyo, Japan) using counter-monochromatized CuKα radiation generated at 40 KV and 100 mA. They were scanned in the range of 2θ from 10 to 60° in a continuous mode at a scanning rate of $2^\circ\ \mathrm{min}^{-1}$. Quantitative analysis was also done during carbonation. Calibration curve for the quantitative analysis was made using separated diffraction peaks of $Ca(OH)_2$(001, $d = 4.905$ Å) and calcite(0–22, $d = 2.095$ Å), respectively.

Morphology analysis

The morphologies of fracture surfaces of the composites after carbonation and washing were examined by means of a scanning electron microscope (SEM, JSM 5400LV, JEOL, Tokyo, Japan) at an acceleration voltage of 15 kV after gold coating. The average NaCl-print size that can be attributed to the pore size existing in the body and hole size formed in pore were analyzed by means of image analysis software (USB Digital Scale V1.0, Scalar Corporation).

Porosity measurement

The apparent densities of the composites after carbonation and washing were calculated from their weight and dimensions. The relative density was calculated by the ratio of the apparent density to the theoretical density of calcite ($2.711\ \mathrm{g\ cm}^{-3}$). The total porosity of the body is defined as follows;

$$\text{Total porosity}(\%) = 100(\%) - \text{relative density}(\%)$$

The total porosity was the average value of five bodies.

Results and discussion

Effect of NaCl content under 2 MPa molding pressure

Figure 1a is the XRD patterns of the composite obtained from the $Ca(OH)_2$/80 wt.% NaCl composite carbonated for 4 h before and after washing with distilled water at 60 °C. It confirms that NaCl was removed totally through washing and $CaCO_3$ body with calcite phase was formed completely within this carbonation time. Figure 1b shows the degree of carbonation of the composites in terms of NaCl content and

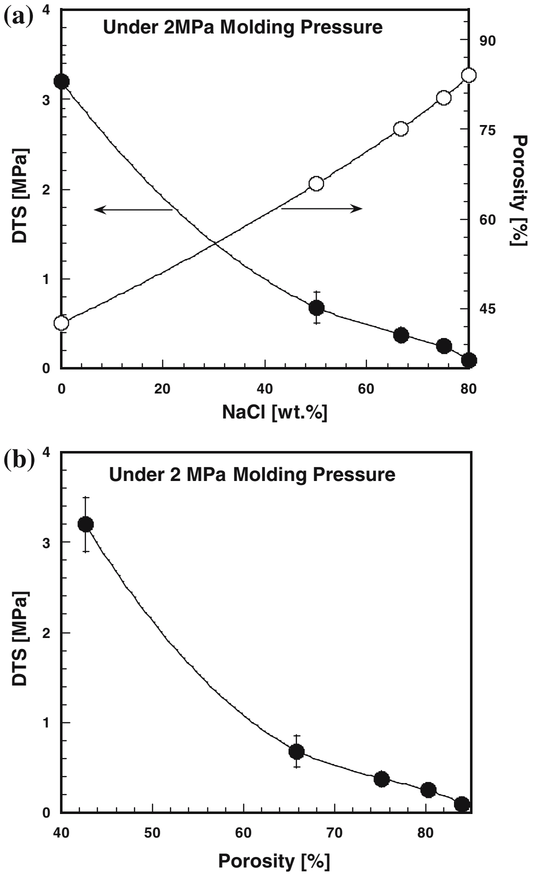

Fig. 3 (**a**) Changes in diametral tensile strengths and porosities of $CaCO_3$ bodies with NaCl content under 2 MPa molding pressure. (**b**) Changes in diametral tensile strengths of $CaCO_3$ bodies with porosity under 2 MPa molding pressure

carbonation time. The time required to transform $Ca(OH)_2$ into $CaCO_3$ reduced with the increase in NaCl content. When the composite was prepared using more than 66.7 wt.% NaCl, $Ca(OH)_2$ was transformed into $CaCO_3$ within 4 h. Whereas, carbonation was remarkably delayed and completed after 72 h for the pure $Ca(OH)_2$ body.

The carbonation of $Ca(OH)_2$ is expressed as the following reaction:

$$Ca(OH)_2 + CO_2 \leftrightarrow CaCO_3 + H_2O$$

CO_2 gas is absorbed in water and NaCl has the property of adsorbing water [28–30]. Consequently, the composites with NaCl get carbonated faster than that without NaCl, because NaCl adsorbs moisture existing in the reaction vessel and this moisture dissolves CO_2 gas, promoting the opportunity of contacting CO_2 with $Ca(OH)_2$. Therefore, the acceleration in carbonation can be attributed to the ability of water adsorbance by NaCl and dissolution of CO_2 into water, which is directly proportional to NaCl content under this molding pressure (Fig. 1b).

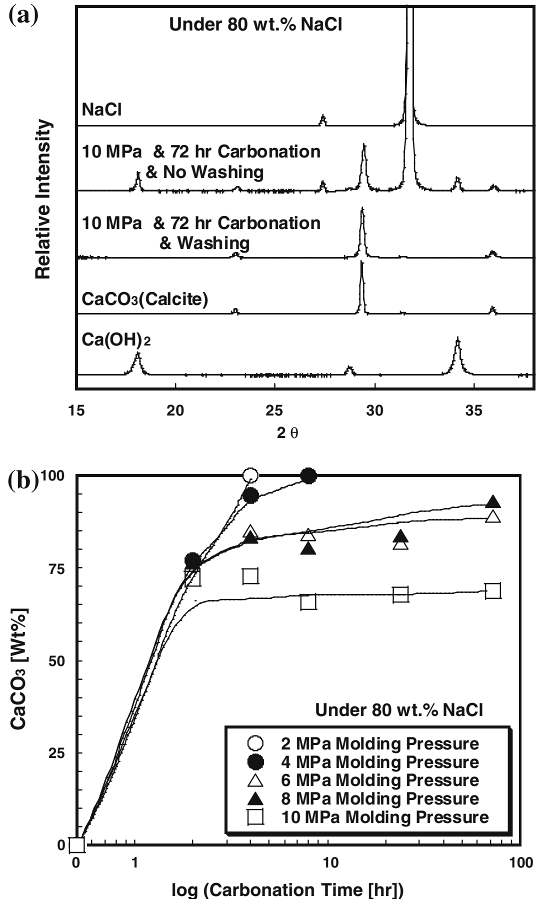

Fig. 4 (**a**) Powder XRD patterns of the $Ca(OH)_2$/NaCl composite containing 80 wt.% NaCl prepared at 10 MPa molding pressure after 72 h carbonation. (**b**) Changes of $CaCO_3$ content in the $Ca(OH)_2$/NaCl composites with carbonation time at various molding pressure under 80 wt.% NaCl

Figure 2 shows the SEM images of fracture surfaces of $CaCO_3$ bodies after carbonation and washing. The fracture surface of the body prepared without using NaCl was dense and compact at this magnification level (Fig. 2a), while NaCl-prints on the bodies prepared using NaCl can be seen clearly (Fig. 2b–e). The NaCl-print size can be attributed to pore size existed in the body and some pores were interconnected through holes that can be revealed from black part in the pores. The degree of existence of pores and interconnection among them augmented more and more with the increase in NaCl content. In case of the body prepared using 80 wt.% NaCl, the average pore size and hole size were 160 and 49 μm, respectively.

Figure 3a shows the change in the porosity and the mechanical strength of the $CaCO_3$ bodies with NaCl content after carbonation and washing. In case of porosity, it was almost linearly increased in proportion to NaCl content. When body was prepared using 80 wt.% NaCl, the porosity was 84%, which is higher than any other body prepared under this experimental condition. However, as

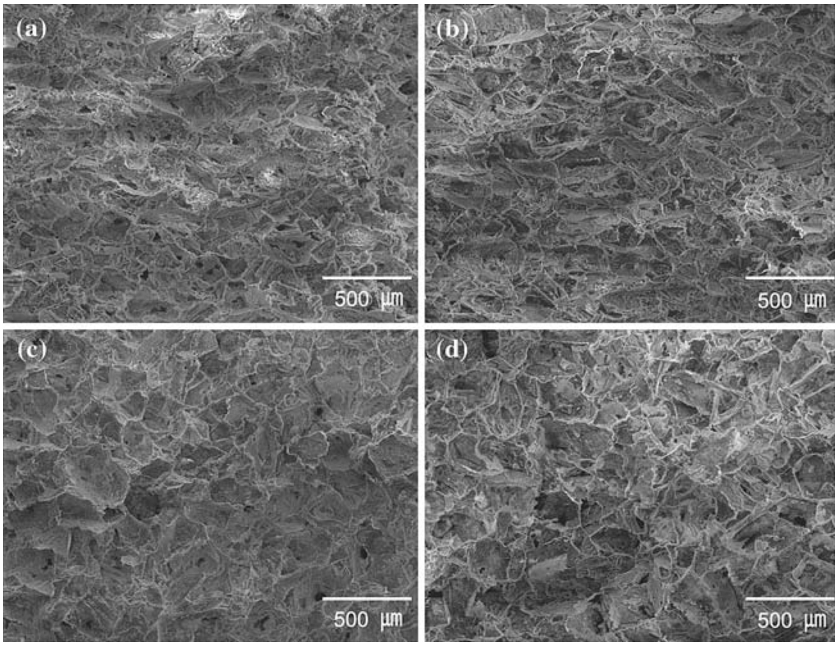

Fig. 5 Scanning electron microscopic observation of the fracture surfaces of $CaCO_3$ bodies under 80 wt.% NaCl. (**a**) 4 MPa molding pressure & 8 h carbonation (**b**) 6 MPa molding pressure & 72 h carbonation (**c**) 8 MPa molding pressure & 72 h carbonation (**d**) 10 MPa molding pressure & 72 h carbonation

expected, it had the lowest mechanical strength. The mechanical strength decreased with the increasing porosity caused by the increase in NaCl content, as shown in Fig. 3b.

We evaluated how much the molding pressure enhances the mechanical strength of the body prepared using 80 wt.% NaCl in the next stage.

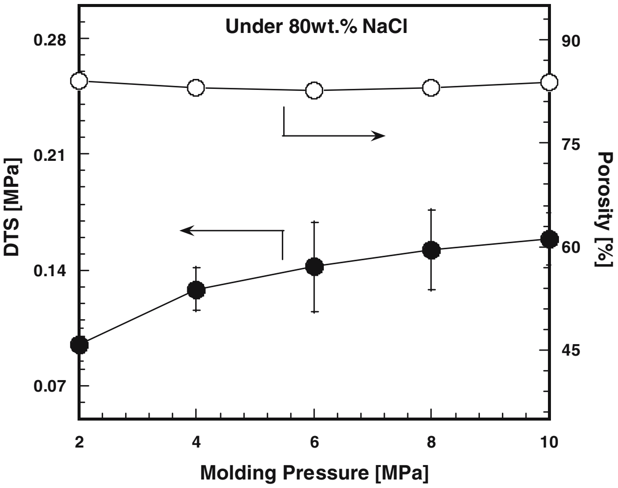

Fig. 6 Changes in diametral tensile strengths and porosities of $CaCO_3$ bodies with molding pressure under 80 wt.% NaCl

Effect of molding pressure under 80 wt.% NaCl

Figure 4a shows the XRD patterns of the composite obtained from the $Ca(OH)_2$/80 wt.% NaCl composite prepared at 10 MPa molding pressure and carbonated for 72 h before and after washing. As shown in Fig. 4a, $Ca(OH)_2$ was not completely transformed into $CaCO_3$ within the

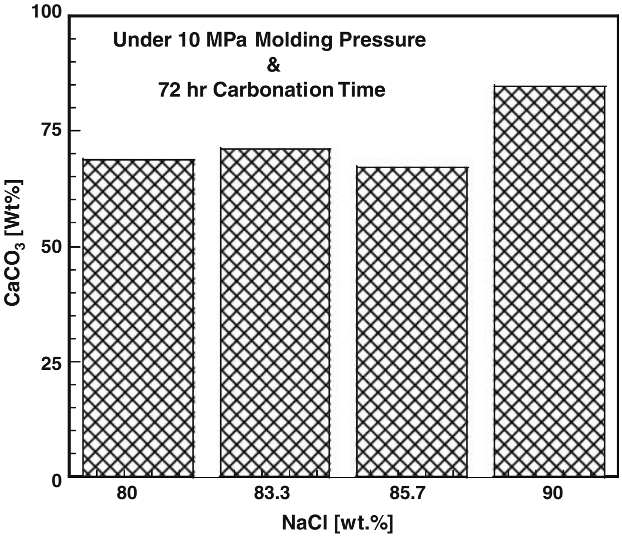

Fig. 7 Changes of $CaCO_3$ content in the $Ca(OH)_2$/NaCl composites at various NaCl content under 10 MPa molding pressure and 72 h carbonation time

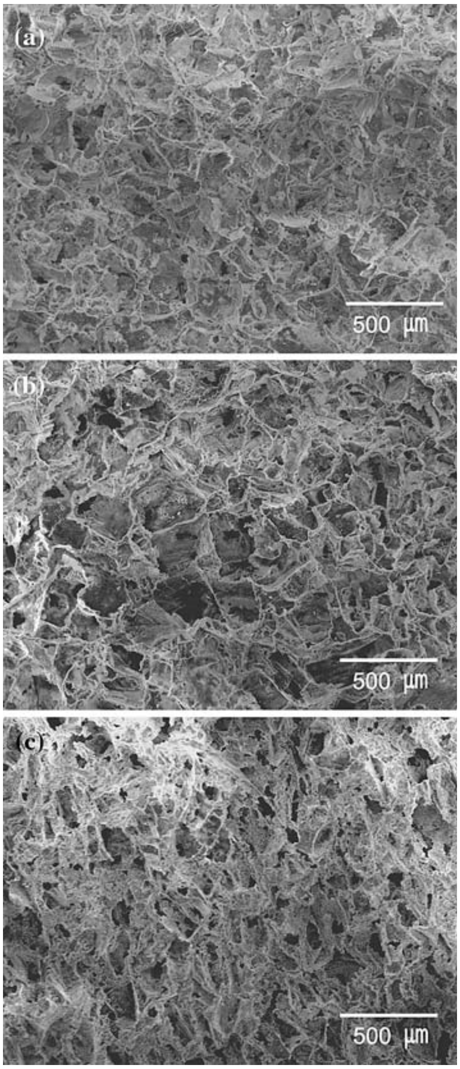

Fig. 8 Scanning electron microscopic observation of the fracture surfaces of $CaCO_3$ bodies after 72 h carbonation under 10 MPa molding pressure. (**a**) 83.3 wt.% NaCl (**b**) 85.7 wt.% NaCl (**c**) 90 wt.% NaCl

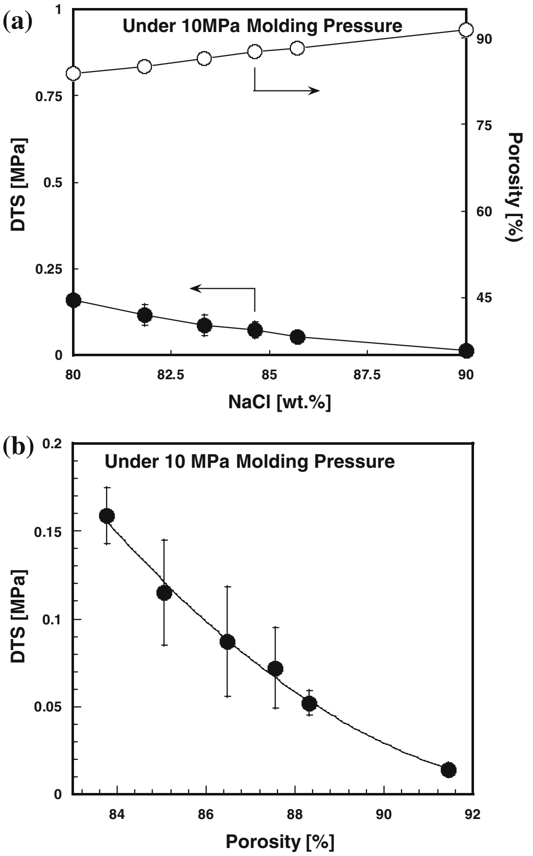

Fig. 9 (**a**) Changes in diametral tensile strengths and porosities of $CaCO_3$ bodies with NaCl content under 10 MPa molding pressure. (**b**) Changes in diametral tensile strengths of $CaCO_3$ bodies with porosity under 10 MPa molding pressure

given carbonation time. However, there was no XRD peak corresponding to $Ca(OH)_2$ in the composite analyzed after washing. Because $Ca(OH)_2$ is soluble in water and, therefore, was removed completely during washing [30]. Fig. 4b shows the degree of carbonation of $Ca(OH)_2$/NaCl composites in terms of molding pressure and time. When the molding pressure was less than 4 MPa, the carbonation of $Ca(OH)_2$/NaCl composite was completed within 8 h. On the other hand, it could not be completed within the given carbonation time when the molding pressure was more than 6 MPa. At the molding pressure of 10 MPa the $CaCO_3$ content in the composite was below 75 wt.%, which was the lowest value under this experimental condition. Actually, the apparent density of $Ca(OH)_2$/NaCl composite prepared at 10 MPa molding pressure was 0.3 g cm^{-3} larger than that of the composite prepared at 2 MPa. Therefore, it is expected that the frame of $Ca(OH)_2$ in the composite and NaCl around this frame was too compact to allow diffusion of CO_2 into the composite or to facilitate carbonation through adsorption of water by NaCl due to high molding pressure

Figure 5 shows the SEM images of fracture surfaces of $CaCO_3$ bodies after carbonation and washing. The average pore size was decreased from 160 μm for 2 MPa (Fig. 2d) to 148 μm for 10 MPa and the average hole size formed in pores also decreased from 49 μm for 2 MPa to 35 μm for 10 MPa, indicating that the body prepared at high molding pressure was dense and compact in comparison with the body prepared at low molding pressure.

Figure 6 shows the changes in the porosity and the mechanical strength of $CaCO_3$ body with molding pressure after carbonation and washing. The apparent density of $Ca(OH)_2$/NaCl composite prepared at 10 MPa molding pressure, as previously mentioned, was higher than that prepared at 2 MPa owing to reduction in the volume of the composite at the molding pressure. Nevertheless, the porosity of the body was maintained almost the same value regardless of molding pressure, which means that there is no significant change in apparent density of $CaCO_3$ body. The reason for almost constant porosity regardless of decrease in volume of the body can be attributed to the removal of $Ca(OH)_2$ that was not carbonated during washing. We found that, though the porosity was almost constant, the mechanical strength of the body prepared at 10 MPa molding pressure was over 1.5 times as high as that of the body prepared at 2 MPa. This can be regarded as the enhancement of the hardness of frame of the body due to the high molding pressure.

We investigated how much the porosity can be increased under 10 MPa molding pressure by manipulating NaCl content in the following experimental stage.

Effect of NaCl content under 10 MPa molding pressure

Figure 7 shows the degree of carbonation of $Ca(OH)_2$/NaCl composites after 72 h in terms of NaCl content. The degree of carbonation was as low as about 70% in the samples containing 80–85.7 wt.% NaCl, while it was 85% in the one containing 90 wt.% NaCl. It is not clear why the degree of carbonation was the highest at 90 wt.% of NaCl content. However, it is probably due to good dispersion of $Ca(OH)_2$ particles in the NaCl matrix at the high NaCl content. This provides easy access for the penetrated CO_2 gas through the NaCl matrix to $Ca(OH)_2$ and causes a high degree of carbonation.

Figure 8 shows the SEM images of fracture surfaces of $CaCO_3$ bodies after carbonation and washing. The average pore size increased from 148 μm for 80 wt.% NaCl (Fig. 5d) to 177 μm and also the average hole size formed in pores was increased from 35 to 80 μm when NaCl content increased from 80% to 90 wt.%, which means that the hole size is dependent on NaCl content. This result supports the above assumption that the reactive surface area of $Ca(OH)_2$ increases with the increase in NaCl content.

Figure 9a shows the changes in the porosity and the mechanical strength of $CaCO_3$ body with NaCl content after carbonation and washing. The porosity increased with NaCl content under 10 MPa molding pressure. This result shows that the body with over 90% porosity can be prepared by using 90 wt.% NaCl. The mechanical strength decreased with increase in NaCl content. Figure 9b shows a relationship between DTS and porosity. DTS decreases with increasing porosity in a similar way as shown in Fig. 3b obtained at lower porosity region.

Conclusions

It was found that $CaCO_3$ body with macropores over 100 μm can be prepared using NaCl as a water-soluble porogen through this new carbonation method and that these macropores can be interconnected without using any kind of connecting agents. Moreover, the body possessing over 90% porosity can be prepared through this method. The carbonation time necessary to completely transform $Ca(OH)_2$ into $CaCO_3$ can be shortened in the presence of NaCl under relatively low molding pressure. Even though the complete transformation was not achieved within given carbonation time when the high molding pressure was employed, pure $CaCO_3$ body is to be obtained through washing the composite carbonated.

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