

Research Article

Hydrothermal Hot Pressing of CaCO_3 -Chitosan Composites with High CaCO_3 Content

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In this study, a hydrothermal hot pressing (HHP) method was used for the preparation of molded composites with high CaCO_3 content. Specifically, composites consisting of chemically synthesized CaCO_3 and chitosan and scallop shells milled with a ball mill were molded by the HHP method; the structures, mechanical properties, and vibration absorption characteristics of the resulting disc-shaped molded composites were investigated. All the composites had high CaCO_3 contents (93%); flexural strengths (several megapascals) comparable to those of limestone and cement; and vibration absorption characteristics (logarithmic attenuation factors of 0.07–0.18) superior to those of aluminum alloys, stainless steel, and ceramics (which have logarithmic attenuation factors of <0.01). The composites prepared from the CaCO_3 -chitosan composites can be expected to find application as light-control materials, as materials for controlling the propagation of light, sound, and vibration waves including vibration-isolating materials and as CO_2 -fixation materials.

1. Introduction

The biominerals that make up structures such as pearls, shells, bones, and teeth are good models for the design of novel functional materials with low environmental loads that can be fabricated by means of environmentally friendly, energy-efficient processes. Pearls and shells, which consist of laminated calcium carbonate and biopolymers, exhibit unique glossy properties arising from the reflection of incident light by the multiple layers, and these laminated structures show high mechanical strength. The process to produce these biomaterials consumes little energy and emits little waste into the environment, and it has an extremely low environmental burden. However, it is difficult to develop industrial processes that mimic the sophisticated, low-energy material-synthesis processes used by living organisms.

Shells are composed mainly of CaCO_3 (95%, plus 5% protein) [1, 2], and CaCO_3 is a useful filler for the fabrication of inexpensive polymer composites. However, such composites become increasingly fragile as the CaCO_3 content increases. In efforts to improve the mechanical properties of such composites, researchers have explored various methods

for mixing CaCO_3 into polymers [3–9], but the maximum content achieved to date is only 64% [9]. The development of polymer composites with higher CaCO_3 content would be an effective way to utilize CaCO_3 as a low-cost filler to produce novel composite materials.

The hydrothermal hot pressing (HHP) method has the potential to be useful for this purpose. The HHP method was devised for producing composites with high mechanical strength by compressing water-containing inorganic powders under external pressure to densify them by squeezing out the water and, at the same time, compacting the particles [10, 11]. In the HHP method, water-containing powdered inorganic compounds in an autoclave under hydrothermal conditions are pressurized from outside the autoclave at a pressure higher than the water vapor pressure inside the autoclave. This treatment promotes compressing of the particles. By means of the HHP method, various powders can be solidified at temperatures lower than 300°C.

In this study, the HHP method was used to prepare molded composites with high CaCO_3 content. Specifically, composites consisting of chemically synthesized CaCO_3 and chitosan and scallop shells crushed with a ball mill were

molded by the HHP method; and the structures, mechanical properties, and vibration absorption characteristics of the resulting disc-shaped composites were investigated.

2. Materials and Methods

2.1. Preparation of CaCO₃-Chitosan Composites. Na₂CO₃ (105.99 g, >99.8%, Wako, Japan) was dissolved in 1 L of ion-exchanged water in a 2 L beaker. CaCl₂ (110.98 g, >95%, Wako, Japan) was dissolved in 0.5 L of ion-exchanged water in another 2 L beaker, and then, a solution prepared by dissolving chitosan (5.00 g, >95%, Wako, Japan) and acetic acid (1.25 g, >99.7%, Wako, Japan) in 0.5 L of ion-exchanged water was added to the CaCl₂ solution to produce a 1.0 M CaCl₂-chitosan aqueous solution. The Na₂CO₃ solution was mixed with the CaCl₂ solution, chitosan, and acetic acid. The mixture was then stirred at either 4 or 95°C for 6 h. The solids were then filtered off and washed with ion-exchanged water. The collected solids were dried at room temperature overnight to obtain CaCO₃-chitosan composites.

2.2. Milling of Scallop Shells. Scallop shells were milled by ball milling for 48 h.

2.3. Molding by the HHP Method. Three samples—CaCO₃-chitosan composites prepared at 4 and 95°C and milled scallops shells—were molded by means of the HHP method at 150°C for 2 h at 56 MPa in the experimental apparatus shown in Figure 1. At the time of molding, enough acetic acid was added to the sample to achieve an acetic acid content of 18 wt.%. The wet sample was heated and pressurized so that the extra moisture was collected in the space for water retreat (see Figure 1). This process produced solid discs with diameters of 60 mm.

2.4. Characterization. Thermal decomposition of the molded composites was evaluated by means of thermogravimetric analysis (TGA; Thermo Plus, Rigaku, Japan). Samples weighing ~5 mg were heated in an open platinum pan under a stream of air (100 mL/min) that was gradually heated to a temperature of 1073 K at a rate of 10°C/min. X-ray diffraction patterns (Cu K α) of samples before and after molding were collected on a diffractometer (RINT-TTR, Rigaku, Japan) operated at 40 kV and 50 mA. Scanning electron microscopy images of samples before and after molding were obtained with a scanning electron microscope (S-3600N, Hitachi, Japan).

2.5. Evaluation of Mechanical Properties of Molded Composites. The molded composites were cut into appropriate shapes, and their flexural strengths were measured by using a device for evaluating mechanical properties (Model 4302, Instron, Japan). Samples were shaped into rectangular cuboids (3 mm \times 4 mm \times 40 mm) in accordance with the specifications of the International Organization for Standardization (ISO 14704, 2000) for flexural tests at a speed of 5 mm/min.

2.6. Evaluation of Vibration Absorption Characteristics of Molded Composites. The molded composites were cut into strips and tapped with a hammer to generate vibrations. Vibration absorption by the samples was measured by means of the laser Doppler method with a laser Doppler vibrometer (LV-1800, Onosokki, Japan).

3. Results and Discussion

3.1. External View. Figure 2 shows an external view of the samples molded into a disc shape (60 mm ϕ) by the HHP method.

3.2. TGA. The CaCO₃-chitosan composites and the scallop shells were subjected to TGA (Figure 3), which revealed successive mass losses due to the removal of absorbed water and acetic acid, degradation of organic compounds, and decomposition of CaCO₃ [12]. The gradual weight loss from 200 to 500°C was due to dehydration reactions of organic compounds. The amounts of CaO and ash produced were calculated from the weight loss when CaCO₃ decomposed into CaO and CO₂ at 600–700°C (this weight loss corresponds to the amount of CO₂ produced) [12]. The overall percentages of CaCO₃ in the composites were estimated to be 93.0, 93.2, and 93.5 wt.% for discs fabricated from the CaCO₃-chitosan composites prepared at 4 and 95°C and the scallop shell disc, respectively; that is, the CaCO₃ contents were high. This is noteworthy because producing nanocomposites containing large amounts of inorganic materials is difficult via conventional mixing processes [13].

3.3. XRD Analysis. XRD analysis of the samples (Figure 4) showed no significant difference between the profiles before and after the HHP treatment (Figure 4). The CaCO₃-chitosan composite prepared at 95°C and the corresponding molded solid were mixtures of aragonite and calcite, whereas the other four samples (before and after molding) were composed solely of calcite [14].

It is supposed that amorphous calcium carbonate was generated by the chemical reaction of calcium carbonate [15, 16]. At low temperature (4°C), the amorphous calcium carbonate was converted to calcite, which is stable in this temperature range. At high temperature (95°C), some of the amorphous calcium carbonate was converted to aragonite, which is stable at higher temperatures [17]. The findings reported herein indicating that calcite formed at low temperature and aragonite at high temperature are consistent with the previously reported results [18].

3.4. SEM. SEM images obtained before and after HHP treatment showed that in the CaCO₃-chitosan composite prepared at 95°C, the acicular crystals of aragonite [19] and the angular crystals of calcite [20] were not changed much by HHP treatment (Figures 5(a) and 5(b)). In addition, in the CaCO₃-chitosan composite prepared at 4°C, a short ribbon-like structure that seemed to be chitosan between calcite with

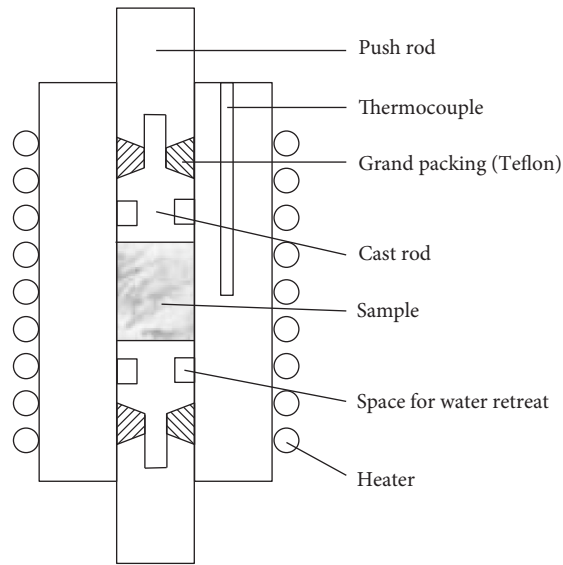


FIGURE 1: Hydrothermal hot pressing system.

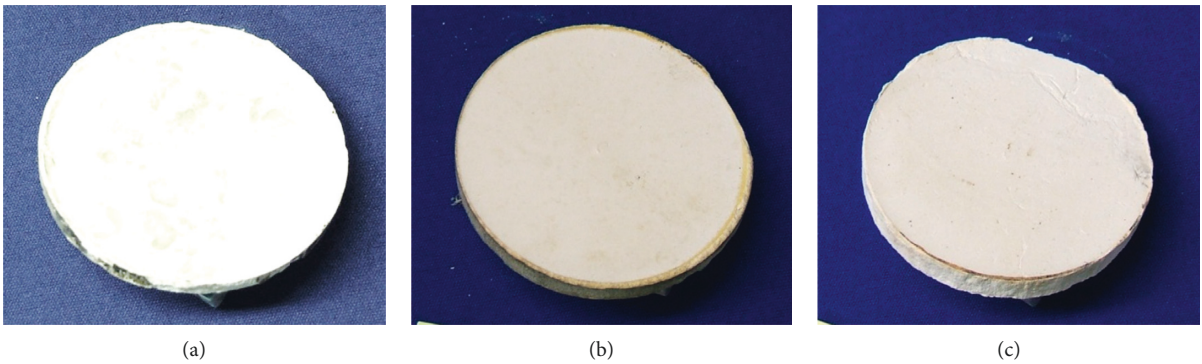
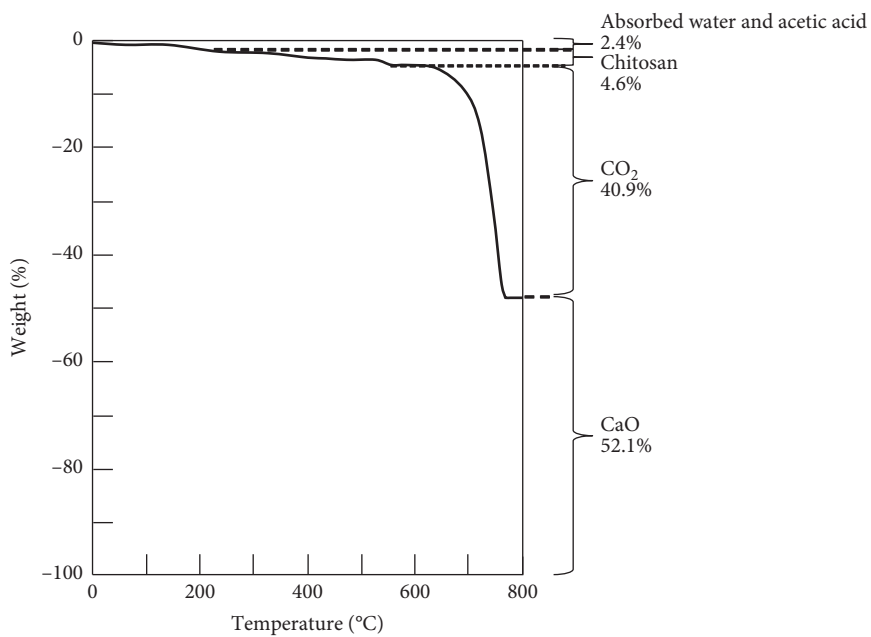


FIGURE 2: Disc-shaped molded composites obtained by hydrothermal hot pressing of (a) CaCO₃-chitosan composite prepared at 4°C, (b) CaCO₃-chitosan composite prepared at 95°C, and (c) milled scallop shells.



(a)
FIGURE 3: Continued.

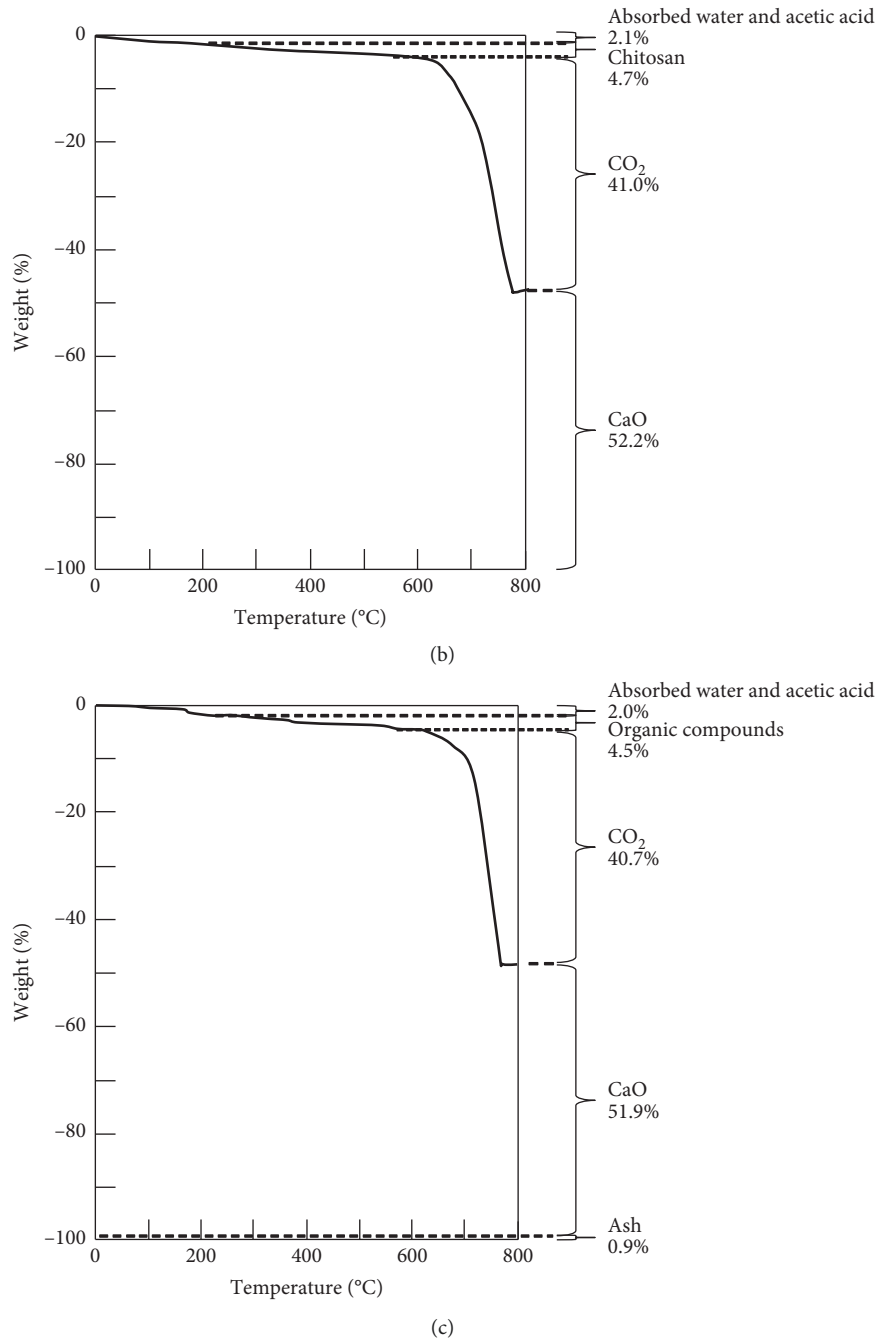


FIGURE 3: Thermogravimetric analysis of molded composites fabricated by means of the hydrothermal hot pressing method from (a) CaCO_3 -chitosan composite prepared at 4°C , (b) CaCO_3 -chitosan composite prepared at 95°C , and (c) milled scallop shells.

several micrometers in diameter showed no significant change upon HHP treatment (Figures 5(c), and 5(d)). In the SEM image of the milled scallop shells, a layered structure peculiar to shells [21] was found, and no significant change was observed after the HHP treatment (Figures 5(e) and 5(f)). These results for the CaCO_3 -chitosan composite prepared at 4°C and the milled scallop sample can be attributed to the stability of calcite under hydrothermal conditions; the calcite was not easily broken down, even during the HHP process [22].

3.5. Mechanical Properties of Molded Composites. The flexural strengths of the molded solids obtained from the CaCO_3 -chitosan composites prepared at 95°C and 4°C and from milled scallop shells were 9.7, 3.8, and 6.0 MPa, respectively (Table 1). Investigation of the mechanical properties of the three molded composites showed that their strengths were 100–255% of the strengths of limestone and cement (with flexural strengths of several megapascals; average 3.8 MPa) [23] and 6–15% of the strengths of glass-fiber-reinforced polymers (with flexural strengths of several

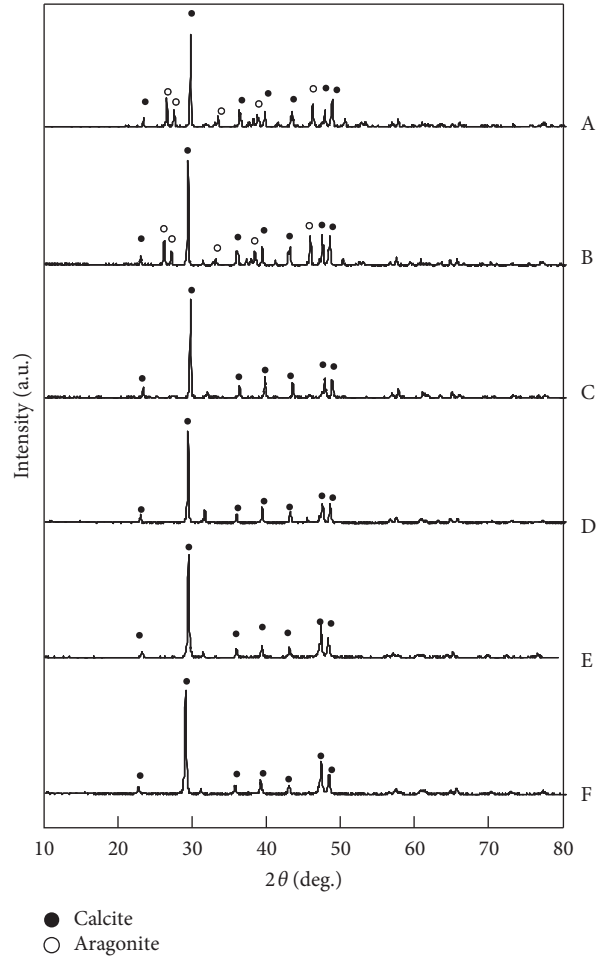


FIGURE 4: XRD patterns before and after hydrothermal hot pressing treatment: (A) CaCO_3 -chitosan composite prepared at 95°C before HHP and (B) molded solid obtained by HHP; (C) CaCO_3 -chitosan composite prepared at 4°C before HHP and (D) molded solid obtained by HHP; and (E) milled scallop shells before HHP and (F) molded solid obtained by HHP.

tens of megapascals; 65 MPa) [24]. The molded solid obtained from the CaCO_3 -chitosan composite prepared at 95°C was particularly strong because it contained aragonite, the orthorhombic system of which forms compact, acicular crystals that make it harder than calcite [25].

3.6. Vibration Absorption Characteristics. The vibration absorption characteristics of the molded composites obtained by the HHP method were evaluated. In plots of the temporal change of the vibration velocity (Figure 6, left panels), it can be seen that all samples showed both rapid swaying and slow swaying with a large amplitude. The amplitude of the envelope of vibration of rapid sway is expressed as [26].

In $A \exp(-\omega_0 \zeta t)$, A is the constant determined by the curve fit; $\omega_0 = 2\pi f_0$, where f_0 is the frequency of rapid sway vibration and ζ is the damping ratio. The amount of attenuation D per second (dB/s) of this envelope is

$$D = 8.686 \omega_0 \zeta. \quad (1)$$

The logarithmic decrement, η , is therefore

$$\eta = 2\zeta = \frac{D}{27.3 f_0}, \quad (2)$$

and it was equated to the magnitudes of the slopes of the blue lines in Figures 6(d)–6(f). The blue lines in Figures 6(d)–6(f) are linear approximations of the nonlinear red lines in Figures 6(d)–6(f).

The calculated logarithmic decrements of the molded solids obtained from the CaCO_3 -chitosan composite prepared at 95°C and 4°C and from milled scallop shells were 0.11, 0.18, and 0.07, respectively (Table 2). The range of the logarithmic decrements of the three samples, 0.07 to 0.18, indicated that the vibration absorption characteristics of the composites were 12–30 times those of aluminum alloys, stainless steel, and ceramics (which have logarithmic decrement of <0.006) [27, 28]. The composites were therefore superior to these alternatives with respect to their vibration absorption characteristics. The trace amount of chitosan in the composites may have absorbed the vibration, acting as a damper.

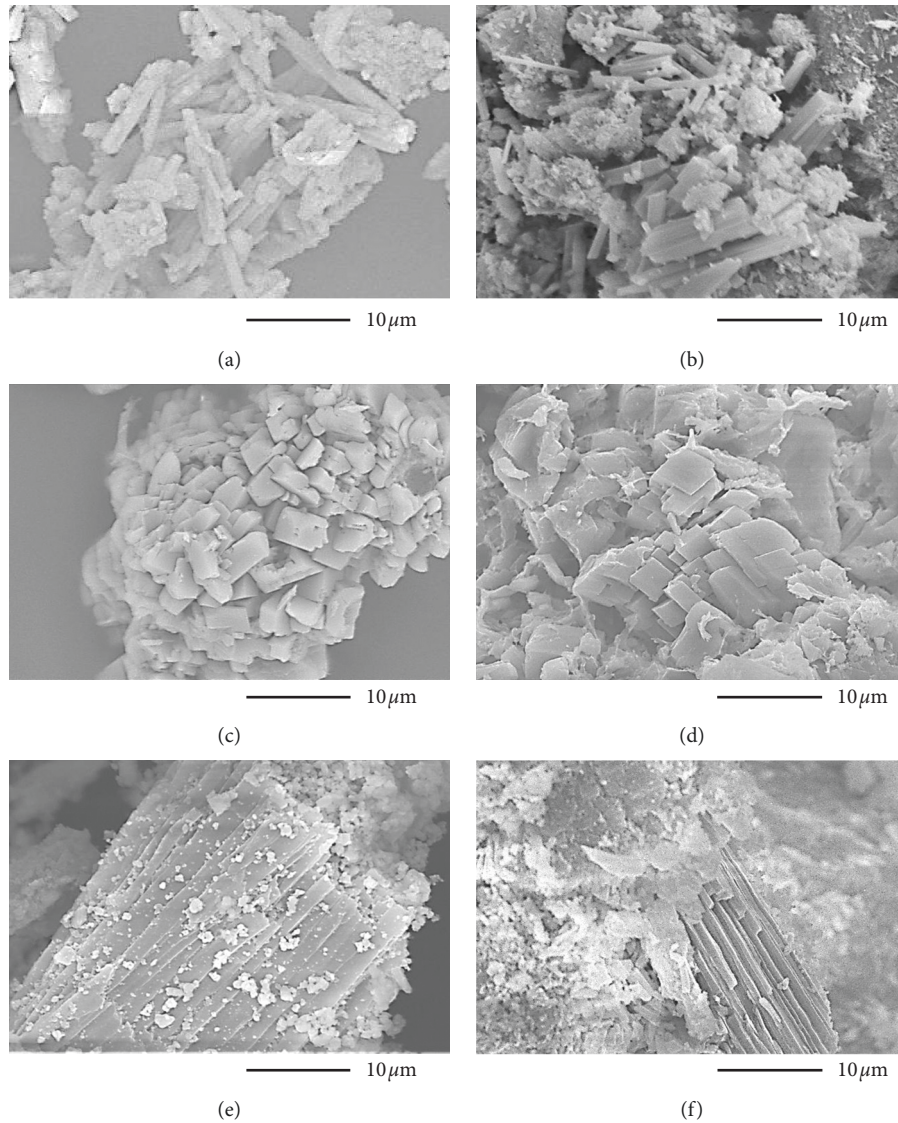


FIGURE 5: Scanning electron microscopy images obtained before and after hydrothermal hot pressing: (a) CaCO_3 -chitosan composite prepared at 95°C before HHP and (b) molded solid obtained by HHP; (c) CaCO_3 -chitosan composite prepared at 4°C before HHP and (d) molded solid obtained by HHP; and (e) milled scallop shells before HHP and (f) molded solid obtained by HHP.

TABLE 1: Flexural strength of molded composites obtained by the HHP method.

	CaCO_3 -chitosan composite prepared at 95°C	CaCO_3 -chitosan composite prepared at 4°C	Scallop shells
Flexural strength (MPa)	9.7	3.8	6.0

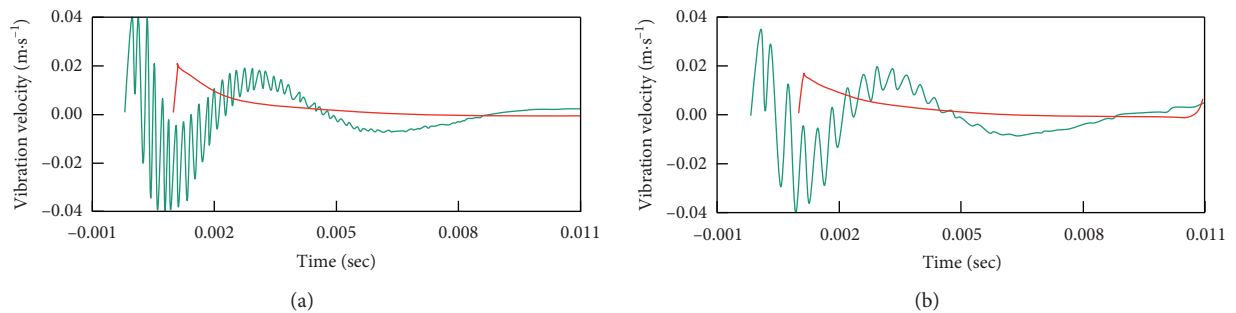


FIGURE 6: Continued.

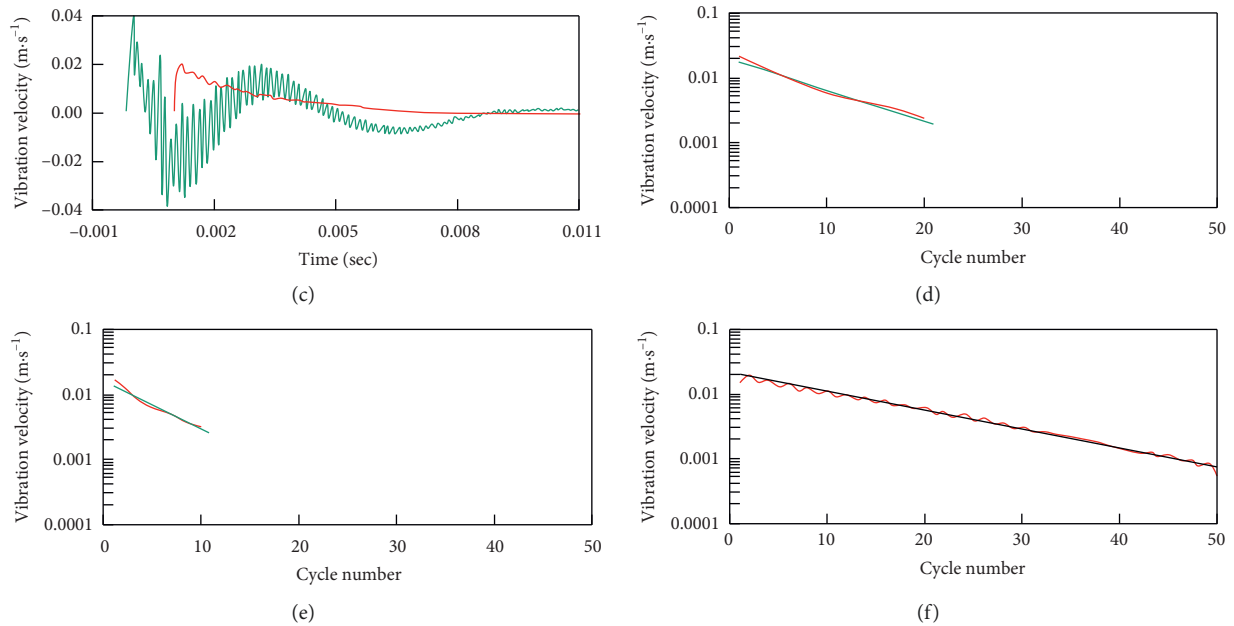


FIGURE 6: Temporal change (left panels) and logarithmic decay (right panels) of the vibration velocity of molded composites obtained by the HHP method from (a, d) CaCO_3 -chitosan composite prepared at 95°C ; (b, e) CaCO_3 -chitosan composite prepared at 4°C ; and (c, f) milled scallop shells. (a–f) The red lines were obtained by subtracting the slow sway from the envelope of the rapid sway, and (d–f) the blue lines are collinear approximations of the red lines.

TABLE 2: Logarithmic decrement of molded composites obtained by means of the HHP method.

	CaCO_3 -chitosan composite prepared at 95°C	CaCO_3 -chitosan composite prepared at 4°C	Scallop shells
Logarithmic decrement	0.11	0.18	0.07

4. Summary

Composites prepared from chemically synthesized CaCO_3 and chitosan and scallop shells milled with a ball mill were molded by means of the HHP method; and the structures, flexural strengths, and vibration absorption characteristics of the resulting molded composites were investigated. The HHP method produced a crystal form of aragonite that had high flexural strength. The complex structure in which CaCO_3 is combined with soft chitosan yields excellent vibration absorption characteristics. The strengths of the high- CaCO_3 -content (93%) composites were 100–255% of the strengths of limestone and cement (with flexural strengths of several megapascals; average 3.8 MPa) and were 6–15% of the strength of glass-fiber-reinforced polymers (with flexural strengths of several tens of megapascals; 65 MPa). The vibration absorption characteristics of the composites were 12–30 times those of aluminum alloys, stainless steel, and ceramics (which have logarithmic decrements of <0.006).

Data Availability

The data used to support the findings of this study are included within the article.

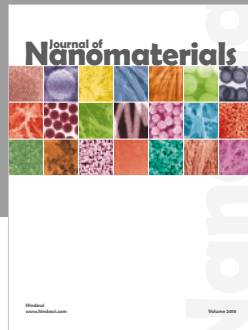
Conflicts of Interest

The authors declare that they have no conflicts of interest.

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