Book Chapter

CaCO$_3$–Polymer Nanocomposite Prepared with Supercritical CO$_2$

Hiroaki Wakayama*

Toyota Central R&D Laboratories, Inc., Japan

*Corresponding Author: Hiroaki Wakayama, Toyota Central R&D Laboratories, Inc., Nagakute, Aichi 480-1192, Japan, Tel: +81-561-71-7861

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Abstract

A novel process for generation of a CaCO$_3$–polymer nanocomposite with a controlled three-dimensional shape was developed. Specifically, a nanocomposite with a high CaCO$_3$ content was produced by introducing supercritical CO$_2$ into a polymer matrix containing Ca ions. A mixture of poly(vinyl alcohol), Ca acetate, and poly(acrylic acid) was poured into a mold, the mold was placed in an autoclave, and CO$_2$ was introduced to precipitate CaCO$_3$ within the polymer matrix. Laser Raman spectroscopy and transmission electron microscopy showed that this process produced a nanocomposite containing highly dispersed CaCO$_3$ (aragonite) nanoparticles. The flexural strength of the nanocomposite was larger than the flexural strengths of limestone and CaCO$_3$ produced by hydrothermal hot pressing. The use of supercritical CO$_2$ facilitated CO$_2$ dissolution, which resulted in rapid precipitation of CaCO$_3$ in the polymer matrix. The above-described process has potential utility for fixation of CO$_2$.

Keywords

Nanocomposite; CaCO$_3$; Supercritical CO$_2$; Mechanical Properties; CO$_2$ Fixation

Introduction

The adverse environmental effects of human activities are becoming increasingly problematic. Minimizing energy consumption and waste generation during materials production is therefore an important goal in the field of materials engineering. One potential strategy for achieving this goal is to mimic processes and simulate materials found in living organisms.
Organisms synthesize inorganic substances such as hydroxyapatite, calcium carbonate (CaCO$_3$), and silica and organic substances such as cellulose and chitin at ambient temperature and atmospheric pressure [1]. These substances are eventually returned to the natural environment and are transformed into resources such as limestone and phosphate ores [2]. In addition, living organisms also serve as sources of materials, such as wood and tree lacquers, that can be used and reused by humans over the course of many centuries [3].

The highly controlled microstructures of living organisms are constructed from various molecular building blocks, and the organisms themselves can therefore be thought of as aggregates of sophisticated nanodevices [4]. By combining multiple types of organic molecules or by combining organic and inorganic molecules at the nanometer scale, organisms can carry out an astonishing array of functions that cannot be achieved with artificial devices.

Biomaterials represent a treasure trove of functional materials, and mimicking biological functions and effectively using biomaterials are major challenges in the field of materials engineering. Biomaterials such as bones, teeth, shells, and pearls are good models for the development of novel functional materials with minimal environmental loads and energy consumption. Designing and creating new functional materials based on substances, structures, functions, and processes of living things are called biomimetic materials processing; and functional materials generated by such processing are referred to as biomimetic functional materials [5]. One biological process that is of particular interest is biomineralization (that is, biological synthesis of minerals). Because this process consumes little energy and emits little waste into the environment, it has an extremely low environmental burden. Therefore, imitation of biomineralization might lead to an environmentally friendly process for synthesis of ceramics.

Biominerals are not simple inorganic crystals but composites of inorganic and organic materials [6]. For example, shells consist of 95% CaCO$_3$ and 5% protein, a composition that imparts
flexibility and structural anisotropy not found in pure CaCO₃ crystals. Several attempts to produce composite materials by mimicking biomineralization have been reported [7-10]. However, in most cases, the CaCO₃ products obtained are powders with particle sizes of no more than a few micrometers. Although there have been a few reports of the formation of CaCO₃ thin films, the process takes several days [11]. More research is necessary for the development of versatile, industrially practical routes to bioinspired materials, such as the production of bulk CaCO₃ nanocomposite materials via rapid CO₂ fixation.

In this study, a novel process for producing CaCO₃ nanocomposite materials was developed. Specifically, glossy CaCO₃–polymer nanocomposites were produced by introducing supercritical CO₂ into aqueous Ca²⁺ in the presence of a polymer. In the work described in this paper, supercritical CO₂ was used to facilitate mineralization of CaCO₃ for production of a CaCO₃–polymer nanocomposite with a controlled three-dimensional shape. Specifically, a mixture of poly(vinyl alcohol) (PVA), Ca acetate, and poly(acrylic acid) (PAA) was poured into a mold, the mold was placed in an autoclave, and CO₂ was introduced to precipitate CaCO₃ within the polymer matrix. Laser Raman spectroscopy and transmission electron microscopy revealed that the resulting nanocomposite was composed of highly dispersed CaCO₃ (aragonite) nanoparticles and had excellent mechanical properties; its flexural strength was larger than the flexural strengths of limestone and CaCO₃ produced by hydrothermal hot pressing.

**Experimental Materials**

PVA (100 g, MW = 2 × 10⁵) was dissolved in 500 mL of 1.42 M aqueous Ca acetate along with 2.4 × 10⁻³ wt% of PAA (MW = 2 × 10⁵). The mixture was stirred for 10 min, heated at 90°C for 3 h, and then poured into a mold. The mold was placed in an autoclave, CO₂ was introduced, and the autoclave was heated at 50°C and 10 MPa for 2 h. The sample was removed from the
mold and cut into a rectangular parallelepiped in order to measure mechanical properties.

**Analysis**

X-ray diffraction patterns (Cu Kα) were collected on a diffractometer (RINT-TTR, Rigaku, Japan) operated at 40 kV and 50 mA. Scanning electron microscopy images and energy-dispersive X-ray spectra were obtained with a scanning electron microscope (S-3600N, Hitachi, Japan). Scanning transmission electron microscopy images were obtained with a transmission electron microscope (JEM-2010 FEF [HR], JEOL, Japan). Thermal decomposition of the samples up to 1273 K was measured with a thermogravimetric analysis instrument (Thermo Plus, Rigaku) under an air atmosphere. Raman spectra were recorded with a Raman spectrometer (NRS-3300, JASCO, Japan). Three-point bending tests were conducted with a testing machine (universal testing machine type 5966, Instron, USA).

**Results and Discussion**

CaCO₃–polymer nanocomposite sample was prepared (Figure 1) via the procedure described in section 2.1.

**Figure 1**: An external view of the CaCO₃–polymer nanocomposite sample.
The CaCO\textsubscript{3}–polymer nanocomposite sample was subjected to thermogravimetric analysis (TGA) (Figure 2). The TGA trace revealed successive mass losses due to the removal of absorbed water and acetic acid, PVA degradation [12], and CaCO\textsubscript{3} decomposition [13] (Figure 2). The weight loss from 200 to 500\textdegree C was due to the dehydration reaction of –OH groups in the PVA chains and subsequent release of CO\textsubscript{2} gas due to degradation of PVA [12]. The amounts of CaO and ash produced were calculated from the weight loss of CaCO\textsubscript{3} (corresponding to the amount of CO\textsubscript{2} produced) when CaCO\textsubscript{3} decomposed into CaO and CO\textsubscript{2} at 600–700\textdegree C [13]. The attribution of the weight loss in each temperature range and the percentages of the total weight contributed by each component are shown in the TGA results (Figure 2). The overall percentage of CaCO\textsubscript{3} in the nanocomposite was estimated to be 57.3 wt%; that is, the CaCO\textsubscript{3} content was high. Producing nanocomposites containing large amounts of inorganic materials is difficult via conventional mixing processes [14].

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure2.png}
\caption{Thermal weight change of the CaCO\textsubscript{3}–polymer nanocomposite sample.}
\end{figure}

The X-ray diffraction pattern of the nanocomposite sample showed only reflections corresponding to aragonite (Figure 3),
Figure 3: X-ray diffraction pattern of the CaCO$_3$–polymer nanocomposite sample.

which is less stable than calcite, the most stable CaCO$_3$ polymorph [15]. The production of aragonite was attributed to the templating effect of the hydroxyl groups of the PVA [16]. That is, the aragonite polymorph formed because the hydroxyl groups bonded to Ca$^{2+}$ via PAA, and the arrangement of the hydroxyl groups was very similar to the arrangement of the atoms of aragonite. When PAA was adsorbed onto the crystalline form of PVA, a locally aligned two-dimensional structure formed in the PVA matrix. The templating effect of the PVA matrix resulted in the formation of aragonite crystals on this two-dimensional structure.

Electron micrographs of the CaCO$_3$–polymer nanocomposite sample were obtained (Figure 4a,b). The image shown in Figure 4a confirmed that ~3-μm CaCO$_3$ particles were embedded firmly in the polymer matrix. The columnar crystals that are characteristic of aragonite [17] were clearly observed in the
magnified image shown in Figure 4b. Surprisingly, calcium was detected at locations both on and near the particles. Specifically, in the energy-dispersive X-ray spectra, calcium was detected both in the smooth areas of the sample and in the areas with CaCO$_3$ particles (Figure 4c,d). This result suggested the formation of a nanocomposite structure consisting of fine CaCO$_3$ particles precipitated in a polymer matrix.

**Figure 4:** Scanning electron microscopy photographs of the CaCO$_3$–polymer nanocomposite sample (a and b) and corresponding energy-dispersive X-ray spectra (c and d).

Figure 5 shows the microscopic laser Raman spectrum of the CaCO$_3$–polymer nanocomposite sample. Peaks for CaCO$_3$ (aragonite) [18] were detected both in the parts of the sample corresponding to CaCO$_3$ particles and in the parts considered to consist mainly of PVA. This result suggested a nanocomposite structure of extremely fine CaCO$_3$ particles precipitated in the polymer matrix and was consistent with the energy-dispersive X-ray analysis result.
Figure 5: Laser Raman spectrum on (a) and near the CaCO$_3$ microparticle (b).

In the transmission electron microscopy image (Figure 6), the presence of fine particles (<10 nm) confirmed that the nanocomposite consisted of highly dispersed CaCO$_3$ nanoparticles in a polymer matrix. The image showed that CaCO$_3$ nanoparticles were dispersed in the PVA matrix (Figure 6). In contrast, as shown in the scanning electron microscopy images (Figure 4a,b), CaCO$_3$ microparticles with dimensions of several micrometers were also present in the samples. The TGA result showed that the content of CaCO$_3$ in the whole sample was relatively high. Even though CaCO$_3$ nanocomposites have previously been synthesized [14, 19, 20], synthesizing nanocomposites with a high CaCO$_3$ content remains challenging. For example, in a previous synthesis of CaCO$_3$ nanocomposites, CaCO$_3$ particles with dimensions of several tens of nanometers, synthesized in advance, were mixed with polymers, but when high concentrations of these CaCO$_3$ particles were mixed with the polymers, the CaCO$_3$ aggregated [21]. In contrast, in this study, the use of supercritical CO$_2$ facilitated CO$_2$ dissolution, which resulted in rapid precipitation of CaCO$_3$ within the polymer matrix. That is, CaCO$_3$-containing nanoparticles with diameters of several nanometers formed in the polymer matrix,
and these nanoparticles were finer than previously reported CaCO$_3$ nanoparticles. The functional groups in the polymer molecules probably acted as templates for the crystallization of CaCO$_3$ in the aragonite crystal structure, and even though the CaCO$_3$ content was high, CaCO$_3$ was highly dispersed in the polymer.

![Transmission electron microscopy image of the CaCO$_3$–polymer nanocomposite sample.](image)

**Figure 6:** Transmission electron microscopy image of the CaCO$_3$–polymer nanocomposite sample.

The flexural strength of the CaCO$_3$–polymer nanocomposite sample was 12 MPa, which is larger than the corresponding values for limestone and CaCO$_3$ produced by hydrothermal hot pressing (Figure 7). The strength of the nanocomposite was likely due to the existence of a nanocomposite structure in which CaCO$_3$ nanoparticles were more firmly attached to the polymer matrix than the particles in limestone or hot-pressed CaCO$_3$. Limestone and hot-pressed CaCO$_3$ consist of calcite, whereas the process reported herein produced aragonite, which is mechanically stronger than calcite [22].
Figure 7: Flexural strength of the CaCO$_3$–polymer nanocomposite sample compared with strengths of limestone and CaCO$_3$ produced by hydrothermal hot pressing.

Conclusion
A novel process for generation of a CaCO$_3$–polymer nanocomposite with a controlled three-dimensional shape was developed. The nanocomposite consisted of large amounts of CaCO$_3$ (aragonite) dispersed in a polymer matrix at the nanometer scale. The nanocomposite had excellent mechanical properties; its flexural strength was larger than the flexural strengths of limestone and CaCO$_3$ produced by hydrothermal hot pressing. The use of supercritical CO$_2$ facilitated CO$_2$ dissolution, which resulted in rapid precipitation of CaCO$_3$ in the polymer matrix. This process has potential utility for fixation of CO$_2$.
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