A New Approach to Organic/Inorganic Composites. Thin Film Coating of $CaCO_3$ on a Chitin Fiber in the Presence of Acid-Rich Macromolecules

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Thin film coating of $CaCO_3$ crystals on a chitin fiber from $CaCO_3$ solution in the presence of an acid-rich macromolecule leads to the fabrication of a novel type of organic/inorganic composites. Molecular interactions between functional groups of these organic matrices play a key role for this control of inorganic crystallization.

In biomineralization processes, the formation of inorganic crystals is controlled by organic biomolecules such as proteins.[1,2] The resultant biominerals have well-organized organic/inorganic composite structures. For example, the nacre of shells has layered structures consisting of oriented flat crystals of $CaCO_3$ and organic thin layers.[1-4]

From the view of materials chemistry, the mimicking of biomineralization by using abundant and relatively low-cost sources may lead to the fabrication of a new type of organic/inorganic composite materials with high performance and environmental benignancy.

It has been reported that insoluble solid matrices such as synthetic polymers and LB films with functional groups give effects on the polymorph and crystal habit of $CaCO_3$.[1,5] Organic additives dissolved in solution also solely affect the $CaCO_3$ crystallization.[6] Moreover, the use of natural components such as extracted proteins or mantle of a shell shows significant effects on the control of $CaCO_3$ crystallization.[7] However, the relationship between the structures of organic matrices and the crystal formation has not yet been fully understood.

Recently, the film formation of $CaCO_3$ crystals was observed in the presence of organic substances, which have simpler structures than proteins.[8,9] A polymer/$CaCO_3$ composite film has been prepared for the combined system of polymer matrices of chitosan and poly(acrylic acid).[8] The cooperation of functional groups of these polymers may play a key role for the control of crystallization. As for hydroxyapatite, thin film coating on organic polymer films and fibers was reported by Kokubo and coworkers.[10]

Here we report successful thin film coating of $CaCO_3$ on a chitin fiber in the presence of acid-rich polymers with simple repeating structures. Chitin was chosen as organic matrix to form organic/inorganic fiber composite because it has functional groups similar to chitosan which was shown to be useful for controlling $CaCO_3$ crystallization with acid macromolecules.[8] Furthermore, chitin is more stable than chitosan. We expected the fabrication of stable fiber composites based on chitin. Poly(acrylic acid) (PAA), poly(L-aspartate) (PAsp), and poly(L-glutamate) (PGlu), which have simple repeating structures, were chosen to function as soluble additives for the crystallization of $CaCO_3$.

$CaCO_3$ was crystallized from supersaturated calcium bicarbonate solution in the presence of soluble and/or insoluble matrices.[11] Rhombohedral calcite crystals of 10 μm in size are formed on the chitin fibers in the absence of soluble polymer additives as shown in Figure 1a. These crystals are typically obtained without organic substances, which shows that the chitin fiber does not solely exert any effects on the crystallization. In contrast, the thin film states of crystals have developed on the chitin fibers in the presence of PAA as a soluble additive in the concentration between 3.6×10^{-4} and 3.6×10^{-2} wt% (Figure 1b), while PAA solely inhibit crystallization of $CaCO_3$. The X-ray diffraction studies show that the crystals consist of calcite and vaterite. It is of interest that the polymorph of $CaCO_3$ switches from vaterite to calcite with the increase of the concentration of PAA. The crystals of 95% or more obtained from the 3.6×10^{-4} wt% solution are vaterite, while only calcite

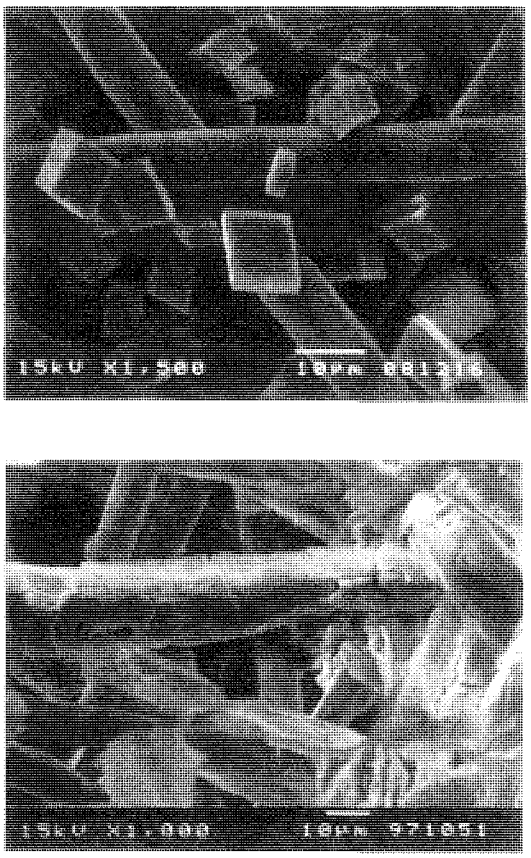

Figure 1. SEM micrographs of $CaCO_3$ crystals on a chitin fiber; (a) in the absence of a soluble additive; (b) in the presence of PAA (2.4×10^{-3} wt%).

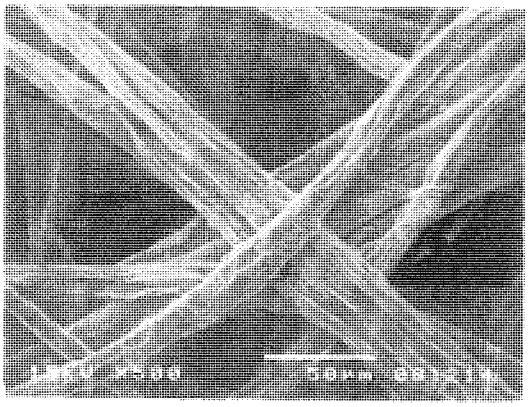

Figure 2. SEM micrograph of $CaCO_3$ crystals on a chitin fiber in the presence of PAsp (4.5×10^{-3} wt%).

is formed for the crystals obtained from the 3.6×10^{-2} wt% solution. Thin films consisting of only vaterite are formed on the chitin when PAsp or PGlu is used as a soluble additive (Figure 2). In this case, polymorph is not dependent on the concentration of these polymers. No film formation is observed in the presence of monomeric compounds such as amino acids and propionic acid, which shows the effect of concentrated functional group of polymers.

Recently, the formation of oriented vaterite aggregates was observed in cross-linked gelatin films containing PAsp though the crystals did not form thin film states.[5c] In this case, entrapped PAsp is considered to induce the oriented aggregation of crystals.

It was suggested that the cooperation of the amide group and the carboxylic acid moiety through hydrogen bonds participates in the strong binding of metal ions such as copper and calcium.[5d,12] Schematic illustration of the binding of the calcium ion on the surface of the chitin fiber is shown in Figure 3. The carboxylic acid of the polymer entrapped on the chitin surface through H bond strongly binds the calcium ion. The local high concentration of the calcium ion on the surface and the inhibition of the growth to the direction vertical to the surface by the adsorbed acid polymers may result in the thin film formation of $CaCO_3$.

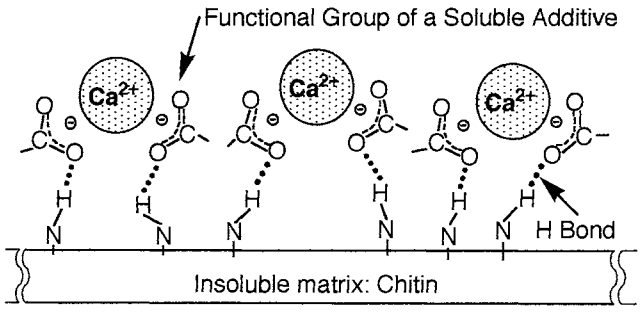

Figure 3. Schematic illustration of the binding of calcium ion on the surface of the chitin fiber through the cooperation of the carboxylic acid of a soluble additive and the N-H group of the insoluble matrix.

We have found that fiber composites are formed by using interactions between two organic polymer matrices which are appropriate for inorganic thin film coating. The approach to novel fiber composites has potential for functional and high performance materials with environmental benignancy.

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11 Poly(acrylic acid) (PAA) was obtained from Aldrich. Poly(aspartic acid) (PAsp) (DP=360) and poly(glutamic acid) (PGlu) (DP=260) sodium salts were purchased from Sigma. A chitin fiber (BESCHITIN® W) was kindly supplied by Unitika Ltd. $CaCO_3$ crystals were grown from supersaturated calcium bicarbonate solution in the presence of organic substances at 30 °C. The detail of the procedure was described previously.[8] The polymorph of $CaCO_3$ was studied with X-ray diffraction measurements. The fraction of vaterite in the crystals was estimated by the Rao's equation: M. S. Rao, *Bull. Chem. Soc. Jpn.*, **46**, 1414 (1973). Scanning electron micrograph images were taken by a JEOL JSM-5400/LV.
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