Layered Thin-Film Composite Consisting of Polymers and Calcium Carbonate: A Novel Organic/Inorganic Material with an Organized Structure

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Layered polymer/calcium carbonate ($CaCO_3$) composite films have been successfully obtained by alternate repetition of spin-coating of polysaccharides and thin film crystallization of $CaCO_3$ in the presence of an acid polymer. SEM images show layered structures consisting of brick of the inorganic crystal and mortar of the polymer.

Organic/inorganic hybrid materials with hierarchical structures have attracted a great deal of attention because high performance and new function can be expected for these materials.[1] Attractive examples for materials scientists exist in biological systems. Biological minerals contain macromolecules and form organic/inorganic composites with controlled microstructures.[1] For example, the nacre of shells has layered structures of brick and mortar, which results in high mechanical and unique optical properties.[1,2] The brick is flat calcium carbonate ($CaCO_3$) crystals and the mortar consists of organic biomacromolecules such as proteins. These bio-macromolecules were shown to be effective to control the crystallization processes of $CaCO_3$ in vitro.[3] If such structures could be synthetically prepared from organic polymers with simpler chemical structures, new materials with high performance and function would be obtained. Intensive research has been focused on the control of the crystal habit, morphology, shape, and size of $CaCO_3$ in the presence of organic substances.[1,4] Recently, the formation of $CaCO_3$ crystals in film states with controlled thickness was achieved in the presence of organic matrices.[5-7] The preparation of thin films of hydroxyapatite, which is another important biomineral, was also reported.[8] However, it is not easy to prepare multi-layered thin films of organic/inorganic composites. Up until now no multi-layered composite based on $CaCO_3$ and organic polymers has been synthetically obtained.

In the present study, we have prepared layered organic/inorganic composites of the $CaCO_3$ and organic polymers, which are a novel type of hybrid materials. The repetition procedure of thin-film crystallization of $CaCO_3$ from aqueous solution after spin-coating of insoluble macromolecules has been employed for the preparation of layered composites. We selected chitin and chitosan as organic solid matrices. Chitin exists in the organic core layer of the nacre, as an insoluble matrix. It is a major component of the exoskeletons of arthropods. Chitosan is obtained by the deacetylation of chitin. We recently reported that the formation of thin film coating can be achieved on the chitosan film and the chitin fiber in the presence of acid-rich macromolecules.[5,6]

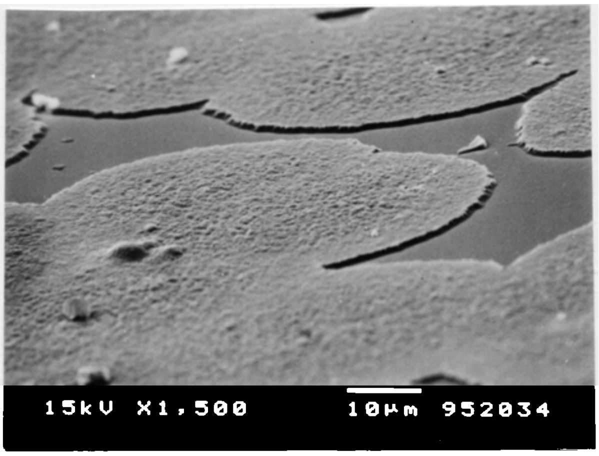

Figure 1. Scanning electron micrograph (SEM) image of developing thin film crystals of $CaCO_3$ on the surface of chitin in the presence of 2.4 x 10^{-3} wt% of PAA.

Thin film crystals of $CaCO_3$ have been developed on these polysaccharide surfaces from supersaturated calcium bicarbonate solution in the presence of poly(acrylic acid) (PAA).[9] In order to obtain polymer/$CaCO_3$ layered structures which mimic those of the nacre of the shells, the control of film thickness and surface flatness is important. Thus, the effect of concentration of the soluble acid-polymers on the crystallization has been examined. Interestingly, $CaCO_3$ crystals have been formed dominantly as flat thin films on the polymer surface, as shown in Figure 1, when the carboxyl-functionalized polymer exists as a soluble additive in a specific concentration range in the solution. Poly(acrylic acid) has induced thin film formation in the range between 2.4 x 10^{-3} and 7.2 x 10^{-3} wt% (3.3 x 10^{-4} and 1.0 x 10^{-3} mol of carboxylic acid/L) on a chitin film. Crystals develop until the surface of the chitin is fully covered with $CaCO_3$. It should be noted that the thickness of the film is successfully kept to be about 0.8 μm, as shown in Figure 1. X-ray diffraction patterns of the crystals show that only calcite is obtained. Sporadic formation of irregularly shaped crystals is observed at concentration ranges lower than those for thin film formation, while no crystal is formed at higher ranges. Similar crystallization process has been observed on the surface of chitosan.

The entrapping of the soluble matrix containing carboxylic acid on the surface of the chitin by the interaction between their functional groups may promote the assembly of the calcium ion and the nucleation of $CaCO_3$. Moreover, the interaction between the poly(acrylic acid) and the $CaCO_3$ crystals suppresses the crystal growth in the direction vertical to the surface.

Layered composite films have been successfully obtained by alternate repetition of spin-coating of the polysaccharide

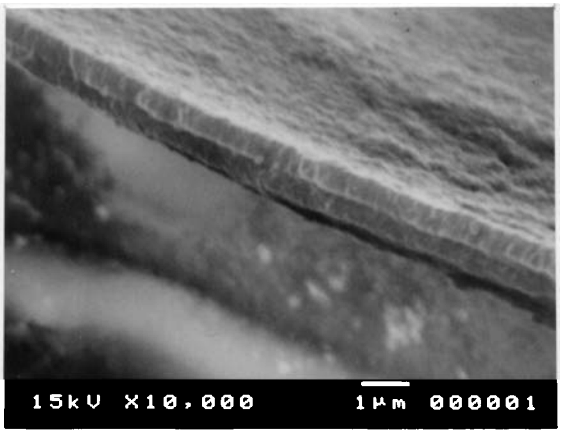

Figure 2. SEM image of the cross-section of a doubly layered composite film consisting of $CaCO_3$ and chitin prepared in the presence of 2.4×10^{-3} wt% of PAA.

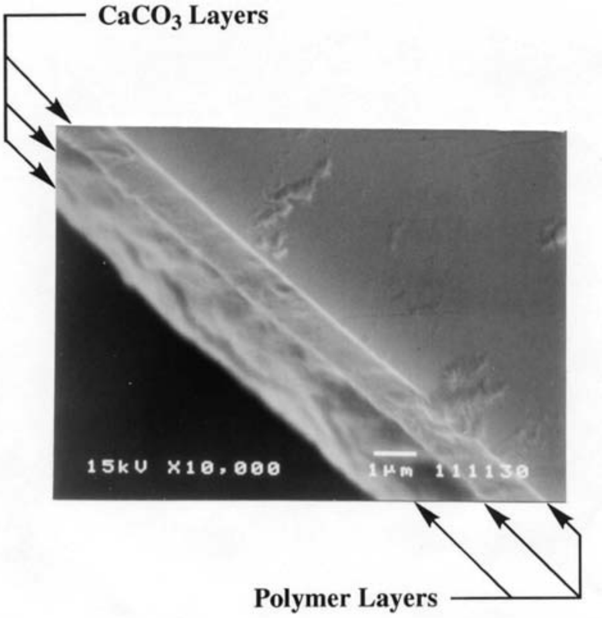

Figure 3. SEM image of the cross-section of a triply layered composite film consisting of $CaCO_3$ and chitosan in the presence of 2.4×10^{-3} wt% of PAA.

and the crystallization of $CaCO_3$. The SEM image of the cross-section of thin film (double layer) (Figure 2) shows the layered structures of the brick of inorganic crystals and the mortar of the polymer. The edge of a triply layered thin composite film obtained by such processes is shown in Figure 3. The second organic thin film layer sandwiched by the inorganic substances is clearly seen in the picture. More precise control of the thickness and the flatness in the crystallization processes may lead to the preparation of multi-layered composite films with high mechanical strength and significant optical properties.

We have achieved the formation of layered composites of $CaCO_3$ and organic polymers by the control of the function of organic substances. These are a novel type of organic/inorganic hybrid materials, which are obtained by co-operation of organic polymers.

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