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Preparation of $CaCO_3$/polymer composite films via interaction of anionic starburst dendrimer with poly(ethylenimine)

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Summary

The $CaCO_3$/poly(ethylenimine) composite film was obtained in the presence of anionic poly(amidoamine) (PAMAM) dendrimer (G=3.5), whereas the formation of composite film was not observed without PAMAM dendrimer or with PAMAM dendrimer (G=1.5) judging from the results of scanning electron micrographs (SEM). The crystal phase of the $CaCO_3$ film formed was found to be calcite by FT-IR and XRD analysis. The adsorption of PAMAM dendrimer on poly(ethylenimine) film might cause local high concentration of calcium ion and induce a formation of the $CaCO_3$ film.

Introduction

Biological organisms produce polymer-inorganic hybrids such as structural materials (shell, bone and wood) and functional materials [1]. These hybrids have superior mechanical properties as compared to synthetic hybrids. For example, nacre of abalone shell is very skill-fully constructed by small amounts of acidic-rich proteins. These proteins consist of water-soluble proteins and water-insoluble proteins that are concerned with mineral crystal nucleation and growth [2]. The insoluble acidic-rich fibrous proteins which consist of glycine, alanine, and phenylalanine take part in a scaffold for crystal nucleation and growth. On the other hand, the soluble acidic-rich proteins consisting of aspartic acid and glutamic acid make a local high concentration of calcium ion to crystallize the minerals. The preparation of $CaCO_3$ films in the presence of synthetic soluble polymers and insoluble matrices has been investigated as a model of biomineralization [3-6]. Zhang et al. reported a crystallization of $CaCO_3$ films on a chitosan film in the presence of poly(acrylic acid) as a soluble additive [3]. Poly(acrylic acid) promoted the formation of $CaCO_3$ films on the chitosan film and also inhibited the crystallization of particle crystal in a solution.

Recently we reported an influence of poly(amidoamine) (PAMAM) dendrimers as additives on the crystallization of $CaCO_3$ particle [7]. The PAMAM dendrimers with carboxylate groups at the external surface denoted as half-generation or G=n.5 dendrimer have been proposed as mimics of anionic proteins. The starburst structures are disk-like shapes in the early generations, whereas the surface branch cell becomes substantially more rigid and the structures are spherical in later generations [8]. It is known that the complexation ability for ion is improved as generation becomes the higher [9]. The PAMAM dendrimers was selected as a model of the soluble acidic-rich proteins to prepare $CaCO_3$ film on a poly(ethylenimine) film. We present here the first example of formation of $CaCO_3$ films in the presence of PAMAM dendrimers.

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Experimental Section

Materials

Poly(ethylenimine) (PEI) with M_w=25,000, poly(amidoamine) (PAMAM) dendrimers, and poly(acrylic acid) (M_w=5,100) were obtained from Aldrich. Calcium chloride and ammonium carbonate were purchased from WAKO Pure Chemical Industries, Ltd.

Characterization

The morphologies of $CaCO_3$ crystals were observed by scanning electron microscopy (JEOL JSM-5310/LV). The polymorphs of $CaCO_3$ crystals were determined by X-ray diffraction and FT-IR (Perkin Elmer system 2000).

Preparation of $CaCO_3$ film

The preparation of $CaCO_3$ film in the presence of PAMAM dendrimer (G=1.5, 3.5) (16, 64 surface carboxylate groups, respectively) was carried out as follows. The crystallization of $CaCO_3$ was carried out by a similar method that described by Addadi et al. [2]. The additive was dissolved in $CaCl_2$ solution, to which carbonate was introduced via a vapor diffusion. The slide glass was treated with H_2O_2-H_2SO_4 cleaning agent for 10 min and rinsed several times with water before use. A poly(ethylenimine) film was obtained by casting poly(ethylenimine) on the slide glass and dried in vacuum. Each of the poly(ethylenimine) film was soaked in a sample bottle (3.5 cm diameter) containing a solution of PAMAM dendrimer in 10 ml of 0.01 M $CaCl_2$ solution. This solution was adjusted to pH 8.5 with NH_3 (aq). One sample bottle containing no PAMAM dendrimer was prepared as a reference for each set of experiments. The sample bottles were placed in a large desiccator. A crushed $(NH_4)_2CO_3$ placed in the desiccator as a carbonate source. After 2 days, the slide glass was rinsed with distilled water, and allowed to dry at room temperature.

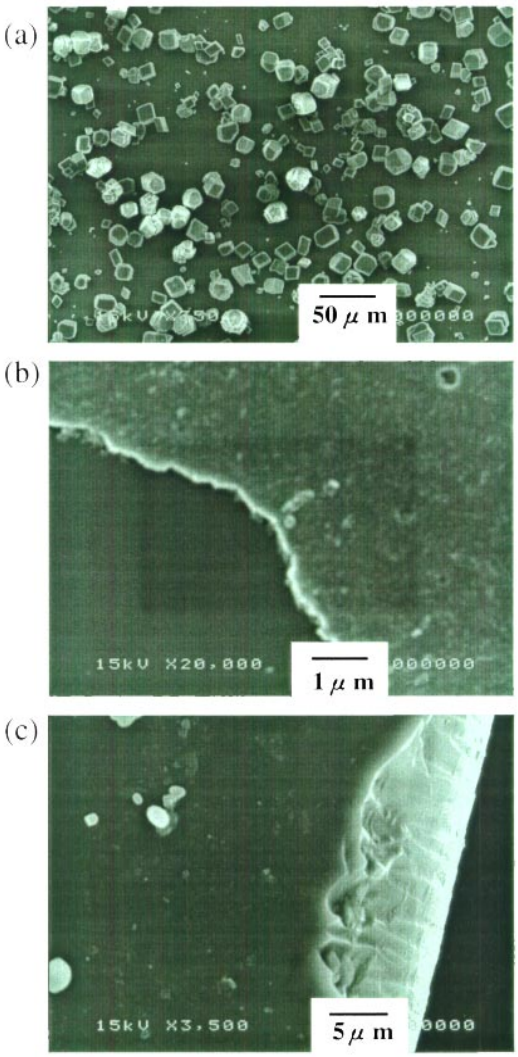

Fig.1 SEM images of $CaCO_3$ composite prepared without PAMAM dendrimer (a), with 0.013 mM PAMAM dendrimer (G=3.5) (b), with 0.063 mM PAMAM dendrimer (G=3.5) (c).

Results and Discussion

From the result of scanning electron micrographs (SEM), $CaCO_3$/poly(ethylenimine) composite

film was found to be formed when an anionic PAMAM dendrimer (G=3.5) was used. On the other hand, no film formation was observed when PAMAM dendrmer (G=1.5) was used or no dendrimer was presented. Figure 1 shows the SEM images of $CaCO_3$ crystals deposited on the slide glass covered with poly(ethylenimine). A smooth $CaCO_3$ films were developed on the poly(ethylenimine) films in the presence of PAMAM dendrimer (G=3.5) [Figure 1(b) and (c)]. In sharp contrast the rhombohedral particles characteristic of calcite were deposited when no PAMAM dendrimers was used [Fig. 1(a)]. The film thickness was roughly estimated from the edge of $CaCO_3$ films by the SEM observation. As increasing the concentration of PAMAM dendrimer (G=3.5), the thickness of the composite film was increased. The crystal phase of $CaCO_3$ film obtained in the presence of PAMAM dendrimer (G=3.5) was characterized by FT-IR and XRD analysis. Figure 2 shows an IR spectrum of the $CaCO_3$ film prepared with 0.013 mM of PAMAM dendrimer (G=3.5) (corresponded to 0.8 mM of –COONa). The bands at 874 and 712 cm^{-1} indicated the calcite formation. The crystal phase of the $CaCO_3$ film with 0.063 mM of PAMAM dendrimer (G=3.5) (corresponded to 4.0 mM of –COONa) was calcite, which was confirmed by XRD. In the presence of 0.013 mM of PAMAM dendrimer (G=3.5), the film entirely consisted of calcite (>99%) (Fig.3). The crystal phase of $CaCO_3$ particles obtained in the absence of PAMAM dendrimer was calcite by FT-IR and XRD analysis.

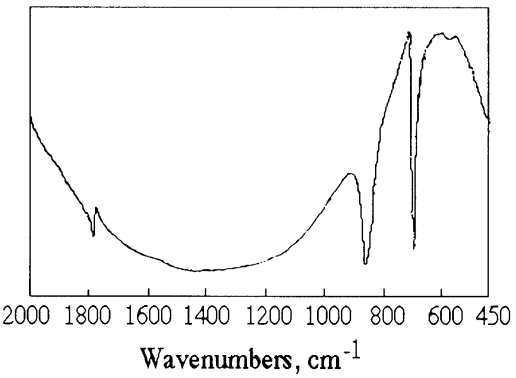

Fig.2 FT-IR spectrum of $CaCO_3$ composite film prepared with 0.013 mM PAMAM dendrimer (G=3.5).

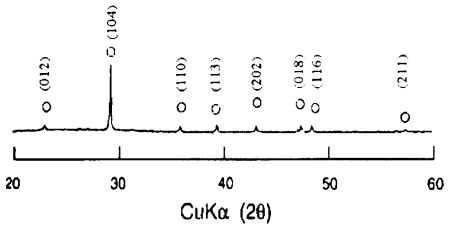

Fig.3 XRD pattern of $CaCO_3$ composite film prepared with 0.013 mM PAMAM dendrimer (G=3.5).

The crystallizations of $CaCO_3$ composite films in the presence of 0.25 mM of PAMAM dendrimer (G=1.5) (corresponded to 4.0 mM of –COONa) and 0.074 mM of Na salt of poly(acrylic acid) (PAA) (corresponded to 4.0 mM of –COONa) were also carried out under the same condition described above. In both cases, the rhombohedral calcite crystals were deposited on the slide glass and the formation of $CaCO_3$ films was not observed.

Fig.4 illustrates that a proposal mechanism of the formation of $CaCO_3$ composite film. The anionic PAMAM dendrimer with calcium ion was adsorbed on the poly(ethylenimine) surface through an electrical interaction to form an insoluble polymer complex. In the absence of PAMAM dendrimer, poly(ethylenimine) should be dissolved in an aqueous phase. These PAMAM dendrimer/poly(ethylenimine) complexes made the high local concentration of calcium ion on the poly(ethylenimine) surface. PAMAM dendrimer prevented the crystal growth to perpendicular direction of poly(ethylenimine) film by an adsorption on the top of the crystal surface. Therefore the

crystal grew and spreaded to horizontal direction of poly(ethylenimine) film.

In the same –COONa concentration, the amount of calcium ions entrapped in PAMAM dendrimer (G=3.5) should be higher than that in PAMAM dendrimer (G=1.5) and PAA. The complexes of anionic starburst dendrimers with calcium ions are considerably stronger for the higher generations than the lower generations as well as PAA. The amount of calcium ions entrapped in the internal coordination site of PAMAM dendrimer with higher generation might be higher than that with lower generation. Accordingly, higher generation of PAMAM dendrimer (G=3.5) inhibits the crystallization of $CaCO_3$ in the solution. Whereas the lower generation of PAMAM dendrimer (G=1.5) and PAA, $CaCO_3$ might be crystallized in the solution and deposited on the slide glass. The inhibiting ability of PAMAM dendrimer was one of the key factors for film formation.

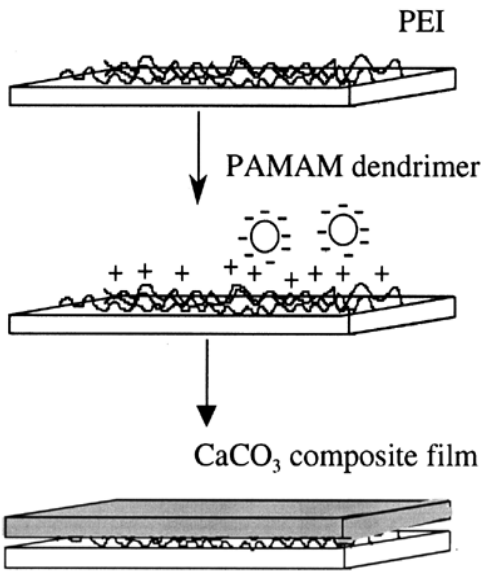

Fig.4 Schematic illustration of the formation of $CaCO_3$ composite film in the presence of PAMAM dendrimer (G=3.5).

In conclusion, the starburst dendrimer (G=3.5) with carboxylate groups at the external surface was proved to be an effective additive for promoting formation of the $CaCO_3$ film on the poly(ethylenimine) surface. The adsorption of PAMAM dendrimer on poly(ethylenimine) film caused high local concentration of calcium ion. Consequently, a nucleation of $CaCO_3$ and a film formation occurred.

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