

Selective Nucleation of Calcium Carbonate Polymorphs: Role of Surface Functionalization and Poly(Vinyl Alcohol) Additive

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ABSTRACT: A model system involving a synthetic polyamide fiber and a water-soluble polymer for the selective nucleation of polymorphs of calcium carbonate crystals under specific experimental conditions is described. The functional groups at the surface of both commercially available and chemically modified polyamide fibers induced calcite nucleation. A water-soluble additive, poly(vinyl alcohol) (PVA), enhanced the selectivity of the polymorph nucleation. The unmodified fiber preadsorbed with PVA molecules induced vaterite nucleation, whereas the chemically modified fiber surface in the presence of PVA nucleated aragonite crystals. Morphological characterization of the polymorphs was done using scanning electron microscope (SEM), and the nature of the crystal lattice was identified using X-ray diffraction studies. Elemental analyses of the crystals indicated the absence of a soluble macromolecular additive inside the crystal lattice. On the basis of these results, a possible mechanism for the nucleation of CaCO_3 polymorphs is proposed.

Introduction

Calcium carbonate is one of the most important building materials in natural hard tissues such as bones and teeth. The composite materials created by biological organisms from calcium salts and proteins are architecturally complex and functionally diverse. These composites are hierarchically ordered into a layer-type morphology and provide superior mechanical stabilities.^{1,2} The organic components of the mineralized tissues are divided into soluble and insoluble matrices.³ It is widely accepted that highly anionic, soluble biomacromolecules, such as proteins/glycoproteins and polysaccharides, play an important role in this process^{4–8} and act as nucleators, growth modifiers, and anchoring units in the mineral formation. The insoluble matrix, such as collagen and chitin, are highly hydrophobic biomacromolecules and form three-dimensional scaffold for facilitating the nucleation of calcium salt crystals. It has been suggested that the soluble acidic macromolecules adsorb onto the surface of the hydrophobic insoluble matrix/scaffolds and play a significant role toward controlling the selectivity of polymorph and crystal morphology during the process of mineralization.^{9,10}

Elegant attempts were focused on the design of synthetic templates to investigate the molecular recognition processes involved in the nucleation of calcium carbonate crystals.^{11–19} Synthetic block copolymers,^{20–23} engineered surfaces,^{24–27} dendrimers,^{28,29} and molecular ribbons³⁰ were used to investigate the nucleation of calcium carbonate polymorphs. We have shown that monolayers of 5-alkoxyisophthalic acid at the air–water interface induced the exclusive nucleation of biologically important aragonite crystals.³¹ Organization of the molecules inside the monolayer and the orientation of

the acid groups at the interface were found to be responsible for such selectivity in the nucleation process. Sulfonated polystyrene and acidic polypeptides induced the nucleation of oriented (001) calcite crystals.³² Falini et al. demonstrated that crystal orientation, aggregation, and polymorphism could be controlled using collagen matrix and acidic polypeptides.^{33,34} Naka et al. showed that addition of acrylic acid as a “latent inducer” induced the nucleation of calcium carbonate polymorphs.³⁵

Here we explore the role of functional groups at the surface of the insoluble matrix (untreated and treated polyamide fibers) toward the selective nucleation of calcium carbonate polymorphs such as calcite, vaterite, and aragonite. The use of polyamide fibers in our experiments was motivated by the fact that the insoluble matrix proteins from prismatic biomineral layer contained polyglycine/alanine domains (Figure 1a).³⁶ Nylon 66 and Kevlar 29 show similar structures in the solid lattice (Figure 1b,c).^{37,38} Also, it is believed that functional groups such as amine, amide, and carboxylic acid are known to significantly influence the mineralization process.³⁹ Chemical treatments of the Kevlar 29 and Nylon 66 fiber surfaces with acid or alkali solutions enhance the charge and polarity on the fiber surface along with the number of functional groups (acid or amino groups). Understanding the cooperativity of functional groups and the adsorbed polymers on the fiber surface toward selective nucleation of calcium carbonate polymorphs is interesting due to its potential in understanding the molecular mechanism of biomineralization processes.

Experimental Methods

Poly(vinyl alcohol) (PVA, 88% degree of hydrolysis) with a molecular mass of 15 000 Da was purchased from BDH Chemicals and used as such in our experiments. Composite grade Kevlar 29 and Nylon 66 fibers were supplied by Dupont

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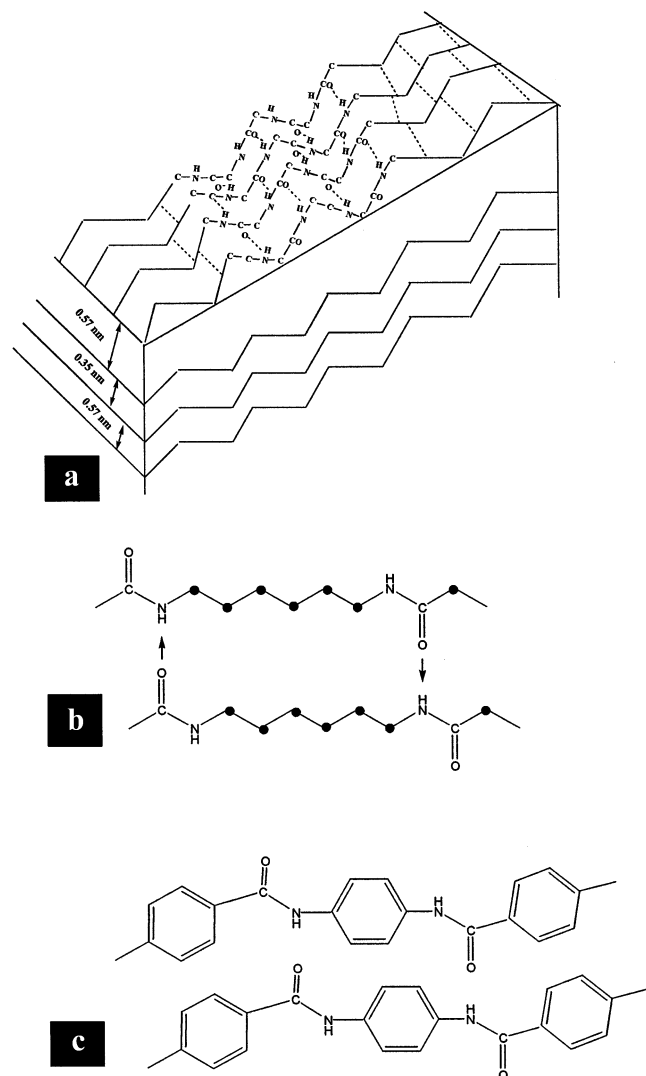


Figure 1. (a) Antiparallel β -pleated sheet of silk fibroin showing poly glycine/alanine domains (redrawn from ref 9), (b) extended structure of Nylon 66, (c) all trans structure of Kevlar 29.

Singapore Pte. Ltd. Water was purified by using a Mill-RO plus system (Millipore) and used in all experiments. CaCO_3 crystals were grown from a supersaturated calcium bicarbonate ($\text{Ca}(\text{HCO}_3)_2$) solution. The solution was prepared by passing carbon dioxide (CO_2) gas for 5 h to a stirred suspension of calcium carbonate in water. The excess calcium carbonate was removed by filtration and CO_2 gas was passed through the resulting clear solution for 1 h to dissolve any residual nuclei formed. The Ca^{2+} ion concentration was calculated using elemental analysis (7.2–7.5 mmol/L). The crystals were grown using small crystallization disks for a period of 96 h, unless otherwise specified. To understand the influence of PVA, aliquots of PVA solution were added to the calcium bicarbonate solution placed in the crystallization disks and the crystals grown at the air–water interface were collected.

For acid and alkali treatments, the polyamide fibers were treated with hydrochloric acid (1.5 N) or sodium hydroxide (1.5 N) solutions for 24 h at room temperature. They were washed thoroughly (i.e., 4 to 5 times) with water, excess water was blotted out, and samples were kept overnight in a desiccator containing phosphorus pentoxide (P_2O_5). Preadsorption of the soluble polymer (e.g., PVA) was done through soaking the pieces of fiber samples in the polymer solutions (concentration; 200 or 2000 ppm) for 24 h, washed with water, dried in an air oven at 40 °C for 3 h and used for crystallization experiments. Growing crystals on the fiber surface was done using the

Table 1. Summary of the Nucleation of Calcium Carbonate Polymorph by Treated and Untreated Fibers Preadsorbed with Water-Soluble Additive PVA

description	polymorphs formed ^a in the presence of fibers preadsorbed ^b with PVA	
	200 ppm	2000 ppm
untreated Kevlar 29	vaterite ($81 \pm 1.5\%$) and calcite	vaterite
untreated Nylon 66	vaterite ($78 \pm 3.0\%$) and calcite	vaterite
acid-treated Kevlar 29	aragonite and vaterite ^c	aragonite
alkali-treated Kevlar 29	aragonite	aragonite
acid-treated Nylon 66	aragonite ($55 \pm 3.0\%$) and calcite	aragonite
alkali-treated Nylon 66	aragonite	aragonite

^a All polymorphs are formed quantitatively, unless otherwise mentioned in the table. ^b Experiment was done by soaking the fibers in PVA solution (200 and 2000 ppm) for 24 h followed by washing with water. After drying, these PVA coated fibers were cut into small pieces and immersed in supersaturated calcium bicarbonate solution for growing the crystals. The percentage of the major polymorph is given in parentheses. ^c Due to the overlapping of the peak, no quantitative estimation can be achieved.

procedure reported elsewhere,⁴⁰ wherein randomly cut fibers (~1 cm in length) were slowly dispersed in the supersaturated calcium bicarbonate solution with or without the macromolecular additives.

Powder X-ray diffraction studies of the crystals were done using a D5005 Siemens X-ray diffractometer with $\text{Cu K}\alpha$ radiation at 40 kV and 40 mA. The samples collected from bulk solutions were slightly crushed using a mortar, placed on a plastic holder, and wetted with a drop of ethanol to form a continuous film. Similarly, the crystals grown on the fiber surfaces were removed carefully and used for further characterization. The phase identification was done by comparing the peak positions in the observed X-ray diffraction pattern of the crystals with the standard data available from Joint Committee on Powder Diffraction Standards. Triplicate experiments were performed to calculate the percentage composition of the polymorphs using Rao's equation.⁴¹ However, due to the overlapping of peaks at the region with low 2θ values, we were not able to estimate the aragonite content in a mixture of aragonite and vaterite crystals. When two polymorphs were observed, the results were reported as major and minor (parenthesis) polymorphs in Table 1.

Morphological studies were carried out using a JEOL JSTM 220A scanning electron microscope (SEM). For SEM observations, the crystals were carefully mounted on copper stubs with a double-sided carbon tape and then sputter coated with gold before examination. Elemental analyses were carried out using Inductively Coupled Plasma (ICP) optical emission spectroscopy model Thermo Jarrel Ash IRIS/AP. In a typical experiment, about 0.3 mg of the calcite crystals were powdered using a mortar and dissolved in 1.5 mL of 3 N HCl in a 2-mL Ependorf microcentrifuge. These tubes were shaken overnight, diluted to 15 mL using water, and analyzed. The ATR-FTIR study was conducted on a Seagull attachment to the Perkin-Elmer Spectrum 2000 spectrometer equipped with a N_2 gas generator and a DTG detector. Untreated, acid-treated, alkali-treated, and PVA treated Nylon 66 fiber bundles were mounted on a ZnSe crystal (45° angle of incidence). A total of 32 scans were collected at a resolution of 4 cm^{-1} .

Results

Effect of Soluble Organic Polymer. Calcite crystals were formed in all our control experiments carried out in the absence of soluble additives or fiber samples (Figure 2a). However, in the presence of PVA (2000 ppm), only aragonite crystals with needle shape morphologies were formed (Figure 2b). X-ray diffraction pattern of the collected crystals confirmed the lattice structure of both phases (Figure 2c).

Effect of Polyamide Fibers. Manoli et al.^{42,43} have shown that elastin and chitin substrates enhance the

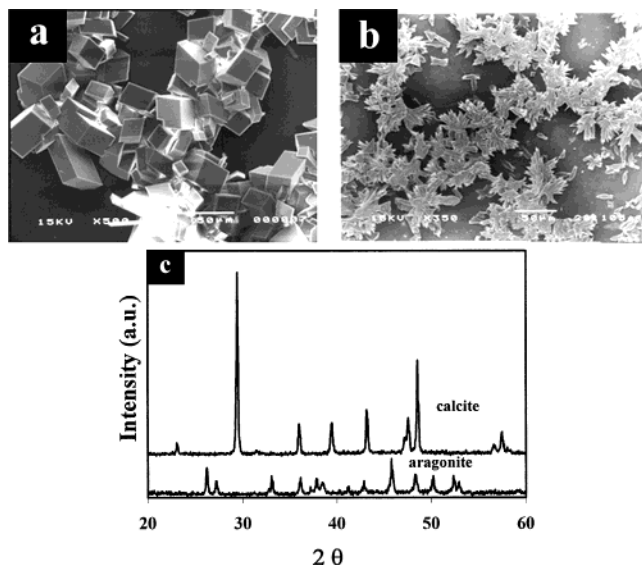


Figure 2. SEM images of the calcite crystals formed in the absence of PVA (a) and aragonite crystals formed in the presence of PVA (b). X-ray diffraction patterns of aragonite and calcite crystals are shown in (c).

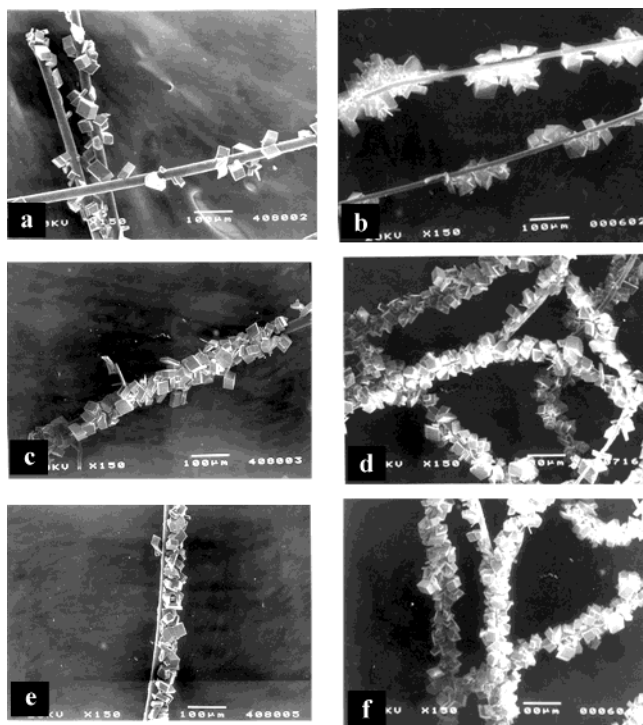


Figure 3. Representative electron micrographs of the calcite crystal growth on: (a) untreated Nylon 66, (b) Kevlar 29, (c) acid-treated Nylon 66, (d) acid-treated Kevlar 29, (e) alkali-treated Nylon 66, and (f) alkali-treated Kevlar 29.

nucleation of calcite crystals due to the presence of $>C=O$ or $>S=O$ functional groups at the substrate. Both Nylon 66 and Kevlar 29 fibers contain amide functional groups at the surface and are expected to interact with calcium ions. The untreated fibers induced nucleation of calcite crystals indicating equilibrium nucleation (Figure 3a,b). When the crystal growth experiments were performed in the presence of acid- or alkali-treated fibers, a remarkable increase in nucleation density (number of crystals per unit area) was

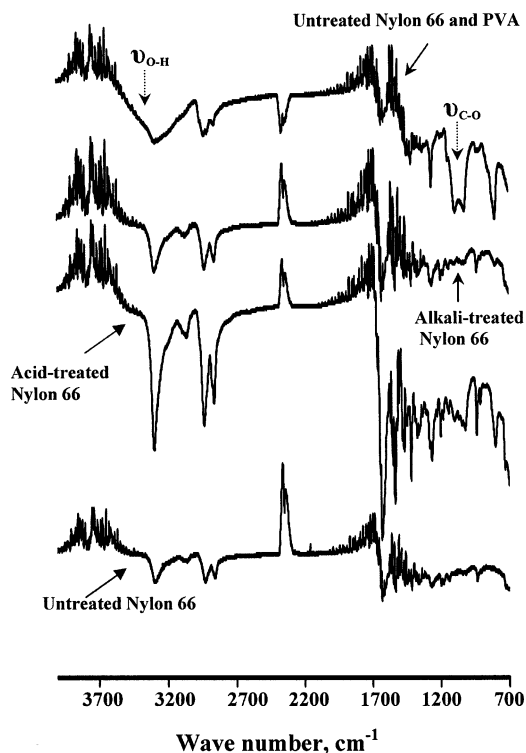


Figure 4. ATR-FTIR spectra of the Nylon 66 fibers.

observed with rhombohedral morphologies (Figure 3c–f). Such high nucleation density on acid- or alkali-treated fiber surfaces indicates that the treatment produced functional surfaces which interact with Ca^{2+} ions more effectively compared to the untreated fiber surfaces. This may be due to the acid- or alkali-catalyzed hydrolysis of the amide groups on the fiber surface. The calcite crystals grew along the length of the fibers without any preferred orientation. ATR-FTIR spectroscopy studies of the untreated, acid-treated, and alkali-treated Nylon 66 is shown in Figure 4. The band at 3290 cm^{-1} and at 1630 cm^{-1} are characteristic of N–H stretching and $>C=O$ stretching vibrations, respectively. These two vibrations strongly depend on hydrogen bonding interactions between Nylon 66 chains. An increase in intensity and broadening of these two bands after acid or alkali treatments are indicative of local micro-environmental changes in the polymer chain.

Role of Soluble Macromolecules on the Fiber Surface. To establish the cooperativity between the soluble additives and the functional groups on the fiber surfaces, the water-soluble PVA was preadsorbed onto the untreated and chemically treated fibers. The appearance of broad band in the IR spectrum around 3300 cm^{-1} (due to $-OH$ stretching) and a peak around 1074 cm^{-1} (due to $C-O$ stretching) indicate the presence of PVA on the fiber surface (Figure 4). It is interesting to note that both the amide bands (3290 and 3060 cm^{-1}) were completely masked after PVA absorption.

The data given in Table 1 clearly indicate the selectivity in the nucleation of a specific polymorph of calcium carbonate. Untreated fibers that were preadsorbed with 200 ppm PVA induced the crystallization of both calcite and vaterite phases. The percentage of vaterite phase present on the Nylon 66 and Kevlar 29 fiber surfaces was found to be 81 ± 1.5 and 78 ± 3.0 , respectively (Figures 6). However, untreated fiber sur-

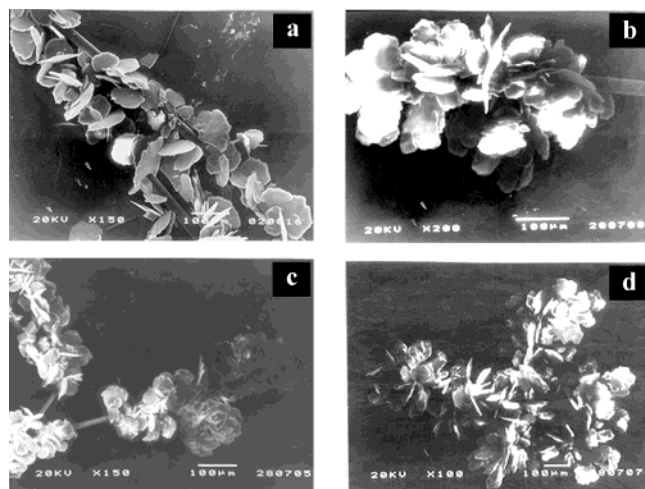


Figure 5. Representative SEM images of the vaterite phase grown on untreated Nylon 66 in the presence of 200 ppm (a) and 2000 ppm PVA (b); untreated Kevlar 29 in the presence of 200 ppm (c) and 2000 ppm PVA (d).

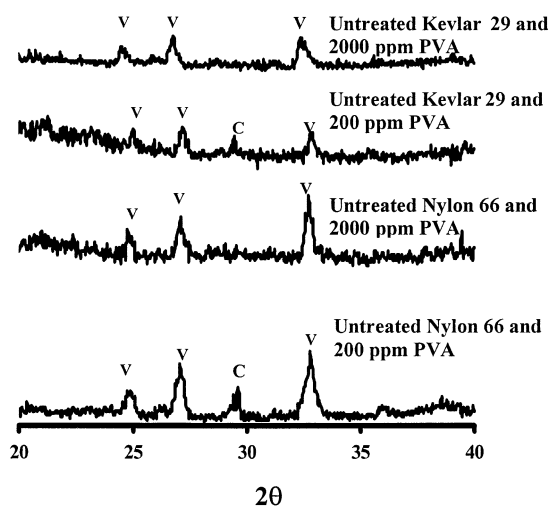


Figure 6. Representative powder XRD patterns of the calcium carbonate polymorphs formed on untreated fibers in the presence of PVA. The diffraction peaks that correspond to calcite and vaterite phases are indicated by C and V, respectively.

faces, at higher concentration of PVA (2000 ppm), nucleated only the vaterite phase (Figure 5) as confirmed by powder X-ray diffraction studies (Figure 6).

When the crystallization was carried out with acid-treated fibers (both Kevlar 29 and Nylon 66) preadsorbed with 200 ppm PVA, a mixture of phases were nucleated. The acid-treated Nylon 66 induced the nucleation of aragonite and calcite crystals (Figures 7a and 8), whereas Kevlar 29 fibers induced the growth of aragonite and vaterite phases (Figure 7c and 8). Since the prominent peaks corresponding to the crystal lattice of vaterite phase overlapped with the aragonite phase, it was difficult to calculate the exact percentage of aragonite phase. On the other hand, the acid-treated fiber surfaces preadsorbed with a higher concentration (2000 ppm) of PVA induced the nucleation of acicular spherulitic aragonite crystals (Figures 7b and 8) on the fiber surface. Similar results were obtained in the presence of alkali-treated fibers preadsorbed with PVA (data not shown). The X-ray diffraction patterns of the

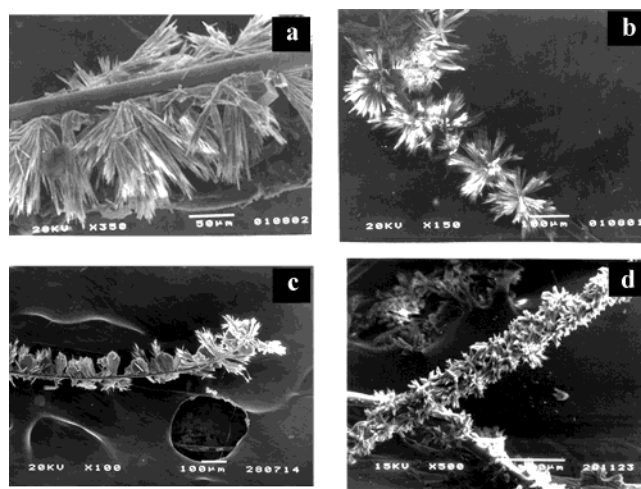


Figure 7. SEM micrographs of the calcium carbonate polymorphs grown on acid-treated Nylon 66 fibers preadsorbed with 200 ppm (a), and 2000 ppm of PVA (b). Acid-treated Kevlar 29 fibers preadsorbed with 200 ppm (c) and 2000 ppm of PVA (d).

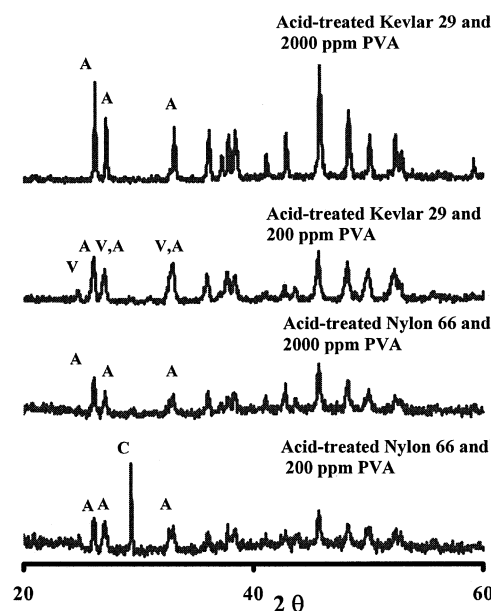


Figure 8. Representative XRD patterns of the CaCO_3 polymorphs grown on fibers preadsorbed with PVA. The letters represent A – aragonite, C – calcite, and V – vaterite.

calcium carbonate polymorphs are given in Figure 8, and all the major peaks are assigned to the corresponding polymorphs.

Discussion

Calcium carbonate exists in three forms, calcite, aragonite, and vaterite. Calcite is the most stable and vaterite is the least stable polymorph. Vaterite crystallizes in a trigonal space group and forms spherical- or floret-shaped aggregates.⁴⁴ However, aragonite exists in an orthorhombic space group and shows a needle-shape morphology.^{45–48} The room temperature precipitation of aragonite requires a large amount of magnesium ions or special proteins.^{8,49,50} The formation of aragonite in the presence of PVA can be explained by the Ostwald step rule in which the less-stable polymorph is formed

first and then subsequently transformed into the more stable phase.⁵¹ However, such transformation could probably be suppressed in the presence of PVA molecules. It is possible that the hydroxyl groups of PVA could adsorb onto the growing crystal face and suppress further growth—a mechanism that was observed in the presence of magnesium ions.⁵²

The observed increase in the nucleation of calcite crystals on the surface of acid- or alkali-treated fibers indicates the importance of surface modification. The formation of vaterite crystals on the untreated fiber surfaces in the presence of PVA shows that the metastable vaterite phase is preferentially stabilized over the more stable calcite or aragonite phases. Under standard conditions, the vaterite phase readily transforms into the stable calcite phase in the presence of water through a solvent-mediated mechanism.⁵³ This process involves dissolution of vaterite crystals followed by nucleation of the calcite phase and generally takes place within 80 h. The absence of such transformations under the experimental conditions employed here indicate that PVA, when adsorbed onto the untreated fiber surface, helps to stabilize the metastable vaterite phase. The stabilization of aragonite on acid- or alkali-treated fibers in the presence of PVA could be due to the change in chemical environment at the fiber surface. It is also known that the formation of the stabilized vaterite phase requires strong Ca–O interaction with the additives or the substrate surface.⁵⁴ The acid or alkali treatment of the fiber surfaces increases the number of polar functional groups such as carboxylate and amino groups, which are known to interact strongly with polar PVA molecules through hydrogen bonds.⁵⁵ This may result in accumulation of more PVA molecules on the fiber surface, which induce the nucleation of aragonite crystals. This was evident from the fact that a mixture of polymorphs were formed on acid- or alkali-treated fibers preadsorbed with a lower concentration (200 ppm) of PVA (Figure 8), as compared to the exclusive nucleation of aragonite at the fiber surfaces in the presence of a higher PVA concentration (i.e., 2000 ppm).

Thus, it is interesting to conclude that in the *absence* of PVA, only calcite crystals were formed in bulk as well as at the fiber surfaces. However, in the *presence* of PVA molecules (preadsorbed on the fiber surface or added in situ), untreated fiber surfaces induced the crystallization of the vaterite phase while aragonite crystals were formed on the acid- or alkali-treated fiber surfaces. A slight loss in selectivity was observed in the case of fibers preadsorbed with PVA, especially at a lower concentration (200 ppm). The results reported here are consistent with the conclusion that added PVA molecules significantly enhance the selective nucleation of CaCO_3 polymorphs cooperatively with the polyamide fibers. Similar cooperativity between the acidic macromolecules and functionalized natural polymers such as, cellulose and chitin, was also observed.²⁴

Selective nucleation of calcium carbonate polymorphs is an interesting area of research. One chemical system involving polyamide fibers and soluble PVA molecules reported here allows us to induce the crystallization of individual CaCO_3 polymorphs using specific experimental conditions. These findings are represented schematically in the Figure 9. In conclusion, we observed the

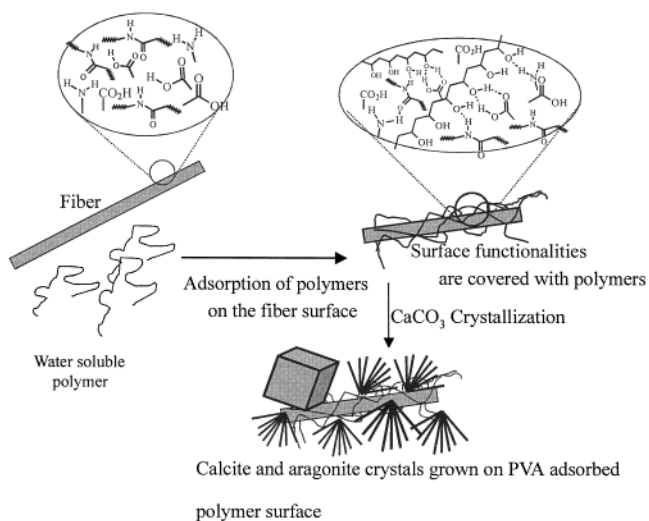


Figure 9. Cartoon representing the molecular mechanism of the nucleation and growth of CaCO_3 polymorphs. The objects are not represented in scale.

following trends: (i) PVA induced nucleation of aragonite crystals in the bulk, (ii) commercially available untreated polyamide fiber surface induced calcite crystals, (iii) acid- or alkali-treated fibers induced the nucleation of calcite crystals, (iv) untreated fiber, in the presence of PVA, gave vaterite crystals, (v) acid- or alkali-treated fibers, in the presence of PVA induced the nucleation of aragonite crystals, and (vi) calcite crystals were nucleated in all control experiments without fibers or added PVA molecules.

The growth of aragonite crystals on the synthetic fiber surface may provide an interesting perspective for designing novel functional surfaces. The organic fibers used in this study are readily available and the fiber surfaces can be modified by simple chemical methods. To the best of our knowledge, the chemical system reported here is an interesting example in which selective nucleation of all three polymorphs of calcium carbonate is achieved under mild conditions.

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