

# Mimicry of Natural Material Designs and Processes

G.M. Bond, R.H. Richman, and W.P. McNaughton

*Editor's Note: From time to time the editor's office receives a manuscript that does not fall into the normal categories of traditional materials engineering. The following article belongs to that group. It reflects the increasing awareness in the*

*traditional materials engineering community of the lessons to be learned from a detailed, microscopic analysis of natural materials and processes. This article is intended to stimulate thought.*

**Biological structural materials, although composed of unremarkable substances synthesized at low temperatures, often exhibit superior mechanical properties. In particular, the quality in which nearly all biologically derived materials excel is toughness. The advantageous mechanical properties are attributable to the hierarchical, composite, structural arrangements common to biological systems. Materials scientists and engineers have increasingly recognized that biological designs or processing approaches applied to man-made materials (biomimesis) may offer improvements in performance over conventional designs and fabrication methods. In this survey, the structures and processing routes of marine shells, avian eggshells, wood, bone, and insect cuticle are briefly reviewed, and biomimesis research inspired by these materials is discussed. In addition, this paper describes and summarizes the applications of biomineralization, self-assembly, and templating with proteins to the fabrication of thin ceramic films and nanostructure devices.**

## Keywords

bone, nanostructures, natural materials, wood, biomimesis

## 1. Why the Study of Biological Systems Could Be Important to Materials Development

TRADITIONALLY, the search for new and improved materials for technology has been guided by inspiration and prediction from physics and chemistry, and by serendipity. In recent years, however, there has been a growing awareness in the materials community that biological systems can provide an additional and valuable source of inspiration. What is envisaged is not employment of natural materials per se in industry, but rather that biological designs or processing approaches, applied to synthetic materials, may offer significant improvements in performance over more traditional designs and fabrication methods.

Biological structural materials (shells of marine creatures, eggshells, wood, bone, insect cuticle, etc.) are complex composite materials. Given the relatively poor properties of the basic building materials, the resultant structures demonstrate remarkable mechanical properties that are central to their required functions. Since there have been tens of thousands of iterations (generations) on the basic designs and fabrication routes for biological substances, we would be remiss not to take advantage of these long-term experiments by evaluating the extraordinary processes that have evolved and how they might be applicable to modern materials synthesis.

In particular, many of these materials exhibit excellent toughness and undergo "graceful failure," that is, the gradual (as opposed to fast) fracture of nominally brittle substances,

during which significant load-bearing capability is maintained until final separation.

In this overview, we use the terms *biomimetic* and *biomimesis* to describe imitations of either the result or the style (Ref 1) of biological systems. Thus, biomimesis in the context used here may involve the structural design alone, or it may include the processing routes that produce these very orderly hierarchical structures.

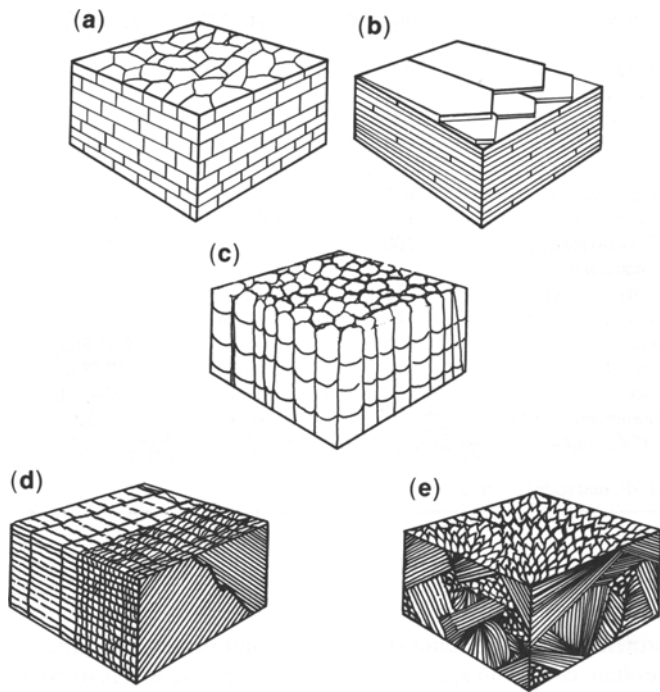
The structures and mechanical properties of various biological composites have been reviewed before (Ref 2-4). Here we survey recent research on the structure, properties, processing, and mimicry of some familiar natural substances. We then examine briefly three special topics in biomimetic processing: thin films, self-assembly, and nanostructures. These are by no means the only subjects of active research on biomimesis. They were selected for their illustrative qualities and their pertinence to our customary endeavors in materials science and engineering.

## 2. Shells of Marine Creatures

### 2.1 Structures and Properties

Among the most widely studied biological structures are those inherent in shells constructed by marine organisms, particularly mollusc shells. The constituents of mollusc shells are, by themselves, not very impressive. These shells consist primarily of calcium carbonate, together with a relatively small amount of organic matrix material (less than 5 wt%). Calcium carbonate is an ionic crystal with relatively low modulus and strength compared to oxide or carbide ceramics. Yet, incorporated into the architecture of shells, the chalky substance exhibits remarkably high flexural and compressive strength, and, unlike man-made ceramics, it is very resistant to fracture. Furthermore, the composite hardness can exceed that of the constituent calcium carbonate minerals (calcite and aragonite), depending on orientation (Ref 5).

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**Fig. 1** Some common microstructures found in molluscs. (a) Nacre. (b) Foliated structure. (c) Simple prisms. (d) Cross-lamellar structures. (e) Complex lamellar structure. Adapted from Ref 2

A driving factor behind research into this field is that if constituent materials with significantly better base properties were fabricated in such a way as to take advantage of the performance-enhancing aspects of mollusc shells, a much-improved constructional material would result.

Various architectures are observed in mollusc shells, as illustrated in Fig. 1. For example, the shell of *Strombus gigas* (pink conch) comprises 99.5 wt% aragonite and 0.5 wt% organic matrix material (Ref 5, 6). A well-ordered, crossed-lamellar structure is seen, with plywood-like lamellae 10 to 40  $\mu\text{m}$  thick (Fig. 1d). The arrangement within this model consists of three levels of lamellae, the orientation of which changes from layer to layer by about 70 to 90°. On the other hand, the shells of abalone (Ref 7, 8) and *Pinctada* (Ref 9) contain nacre, which is constructed of small platelets of calcium carbonate stacked in brick-and-mortar fashion (Fig. 1a). The platelets in *Pinctada* are about 300  $\mu\text{m}$  thick, with an aspect ratio of about 8.

Different mollusc shell architectures provide different combinations of properties. For example, nacreous shells generally have higher strengths and work of fracture than crossed-lamellar shells (Ref 9-13). It has been pointed out, however, that the more common crossed-lamellar structure is better able to arrest a running crack (Ref 13), with obvious survival value for the shell's inhabitant. When graceful failure is observed in marine

shells, it is associated with evidence of crack deflection, crack branching, and lath pullout, all directly attributable to the architectural features shown in Fig. 1. The high work of fracture in nacre is also attributed, in part, to extensive delamination at large distances ahead of the crack tip, as well as shearing and ligament formation in the organic matrix (Ref 13, 14).

## 2.2 Processing

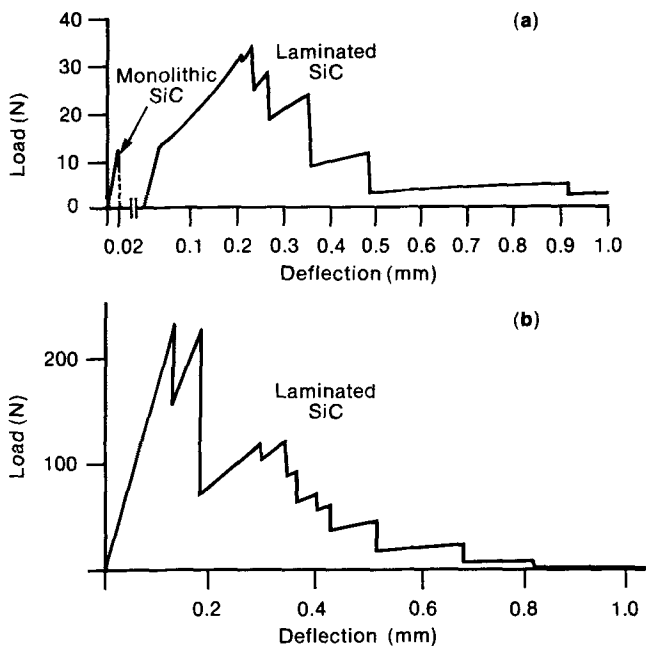
How biomineralization occurs in different organisms has been the subject of a considerable body of literature (see, for example, Ref 15-19). Although many of the details of biomineralization are not yet well understood, the processes involved are of considerable interest for man-made materials. In particular, marine creatures control the following aspects of nucleation and growth in biominerals: nucleation is induced in certain locations and prevented elsewhere; the phase of the mineral deposited on the substrate is determined; and the sizes, shapes, and orientations of the crystals are controlled. The complex composite architectures observed in marine shells are made possible by the ability of the systems to direct the nucleation and growth of the mineral crystals, and this control is attributed to the organic material present.

While the details of deposition vary from system to system, certain generalizations can be made (Ref 20). Deposition appears to be controlled by nucleation proteins, typically polyanions, which are glycoproteins rich in amino acid residues. All the identified nucleation proteins are water soluble and contain many negatively charged functional groups. In addition to this chemical control, the sizes and shapes of crystals are almost certainly influenced physically by the presence of sheets of organic materials. Over and above the effect of organic sheets between crystals, it has been suggested (Ref 21) that the sizes and angular spreads of perfect domains within single crystals are controlled by organic layers that are intercalated between the domains.

There are several aspects to the interaction between organic and inorganic phases as it is currently understood. It is believed (Ref 22, 23) that the fixed polyanions assist nucleation by providing a negatively charged surface that interacts electrostatically with cations (here, calcium). In addition, the distribution of the polyanions on the substrate may provide a stereochemical "template" for adsorbing a layer of cations, thus controlling both the phase and orientation of the nuclei, as well as their location. It is also believed that the polyanions in solution can influence crystal shape by selective adsorption onto certain crystal faces (Ref 23-25). The macromolecules are thought to "recognize" certain stereochemical motifs on these crystal faces, adsorb onto them, and thereby inhibit further growth on those faces. Extensive efforts are being made to elucidate the mechanisms of molecular recognition involved both in crystal nucleation and in adsorption onto crystal faces (Ref 26-29).

## 2.3 Biomimesis of Marine Shells

Aspects of nacreous shell architecture have been mimicked with man-made materials several times. In one investigation involving aluminum/boron carbide ( $\text{Al}/\text{B}_4\text{C}$ ) cermets, two approaches were tried. One produced laminates of  $\text{B}_4\text{C}$  sheets separated by thin aluminum layers; in the other, tapes of  $\text{B}_4\text{C}$



**Fig. 2** Load-deflection curves for monolithic and biomimetic laminate materials. (a) Notched. (b) Unnotched. Adapted from Ref 31

were stacked, laminated under pressure and temperature, sintered, and subsequently infiltrated with aluminum to produce a “graded” microstructure (Ref 30). Samples from the first approach with aluminum layers had higher strength but lower fracture toughness than conventional Al/B<sub>4</sub>C composites. The lower toughness was attributed to discontinuities in the aluminum layers caused by processing. Graded laminates, in contrast, showed increasing strength and toughness with decreasing lamina width. The highest values obtained were 945 MPa and 14 MPa m<sup>1/2</sup>, about 40% higher than for monolithic material.

Innovative experiments inspired by the structure of nacre in shells of the mollusc *Pinctada margaritifera* were reported recently (Ref 31). Laminar composites of silicon carbide (SiC) and graphite were fabricated from rolled sheets of fine-grained β-SiC (1.3 μm average grain size, with about 5% of α-SiC to control grain growth) coated with a suspension of colloidal graphite. Stacked sheets were compacted and sintered without pressure. The SiC layers were each 150 μm thick, separated by graphite layers that were purposely varied over the range 3 to 25 μm. Fracture surfaces of the sintered bodies revealed that the interfaces between SiC laminae are made up of small graphite plates, with the planes of the platelets preferentially oriented in the plane of the interface. Failure in bending occurs by successive crack advance across a lamina, followed by crack deflection along the next graphite layer (that is, graceful failure) (Fig. 2). The lesson here would appear to be that even unsophisticated mimicry of natural architectures (fine-grained SiC substituted for calcium carbonate, graphite substituted for the soft

**Table 1** Synthetic and natural ceramics

Material	Tensile modulus, GPa	Bend strength, MPa	Work of fracture, J/m <sup>2</sup>
Alumina	300-350	100-1000	7-35
Fused silica	72	...	9
Porcelain	90-110	130-150	17
Pyroceram	114	300-400	50
Silicon nitride	280-310	300-1000	40-70
Silicon carbide	370-410	750-850	20-40
Zirconia (stabilized)	165	140-350	35-40
Zirconia (partially stabilized)	200	1200-1400	200-300
Portland cement	12	11	20
MDF cement	40	150-250	200
Jade	205	60-78	270-985
Enamel	45	76	12-200
Nacre	64	130	600-1240
Biomimetic laminate (SiC/graphite)	...	633	6150

MDF, macrodefect-free

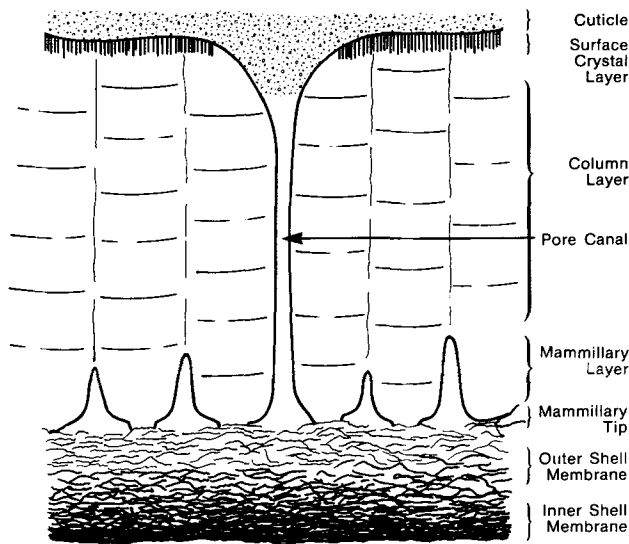
protein layers in marine shells) can result in much-improved ceramic composites, even without the exquisite levels of control exercised in biological processing.

The laminated structure of abalone shells was the inspiration for a family of composites called MIMLCs (micro-infiltrated, micro-laminated composites), which consist of thin layers of ductile, high-toughness material alternating with a hard, brittle, low-toughness substance in thin layers (Ref 32). An MIMLC composed of nickel and alumina-nickel cermet was tested as an armor material against heavy-alloy penetrators, with promising results. Cracks generated in the cermet were deflected by the thin nickel layers between the cermet layers. A similar composite design (e.g., cobalt/tungsten carbide) was proposed as the basis for improved cutting tools (Ref 32).

The architecture of mollusc shells, based on microcrystals of calcium carbonate and a protein-rich organic matrix, also inspired the development of “flexible” or macrodefect-free (MDF) cement (Ref 33). Although it is strong in compression, ordinary cement is weaker in tension than mollusc shells by more than an order of magnitude. Inclusion of a water-soluble polymer in the formulation (to mimic the slurry of protein and complex sugars that acts as the mortar in mollusc shells), together with the minimum amount of water necessary for the hydration reaction, resulted in a cement that was free of the usual 1 mm pores and that was an order of magnitude stronger in bending than conventional pastes: more than 200 MPa compared to about 10 MPa.

#### 2.4 Comparison of Natural and Synthetic Ceramics

Table 1 compares natural and man-made ceramics. Several of the entries are taken from a similar table by Calvert (Ref 34). Some other constructional materials, either found in industry (cement, electrical insulators) or suggested for future applications (thermal-barrier coatings, high-temperature heat exchangers) have been added. It is seen that the toughness of natural materials (jade, enamel, and nacre) stand out, as do



**Fig. 3** Schematic diagram of radial section through the integument of the hen eggshell. Adapted from Ref 43

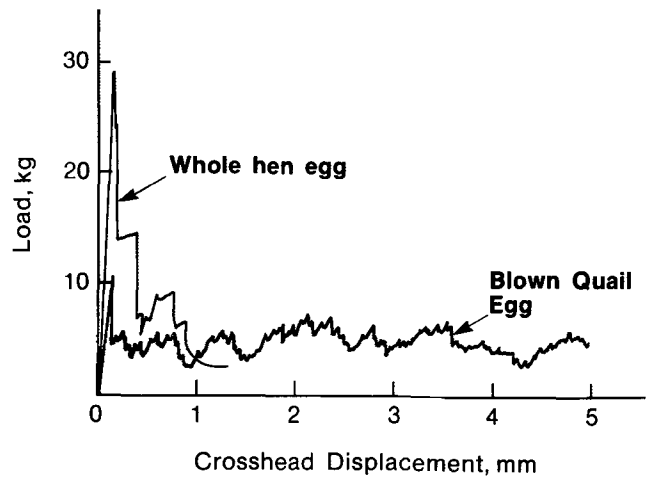
those of the biomimetic composites MDF cement and SiC-graphite.

### 3. Avian Eggshells

#### 3.1 Structures and Properties

The egg integument of avian species consists of the calcareous shell (mainly calcium carbonate in the form of calcite) and the membranes that line the inside of the shell, shown schematically in Fig. 3. The inner portion of the shell comprises many dome-like projections (the mammillary or cone layer), the tips of which are embedded in the outer portion of the shell membrane, with intimate attachment between mammillary tips and membrane fibers. The column or palisade layer is made up of linear arrays of similarly oriented calcite prisms that extend the full thickness of the column layer. There is some evidence that each column consists of many platelike crystallites (parallel to the shell surface) with fairly similar orientations. This is covered in many (but not all) species by a thin, distinct layer of small crystals. In some species there is also a thin organic cuticle and/or an inorganic cover layer on the outer surface of the shell.

Although the hen eggshell is an essentially brittle material (Ref 35), it was discovered that the egg integuments of some avian species are not (Ref 36). In compression tests of quail eggs, for example, the drop in load at the onset of fracture was proportionally much smaller than for hen eggs, and it was followed by a series of peaks and troughs in the load-versus-displacement curves. The loads sustained at the peaks were as much as 70% of the load required to initiate failure. Figure 4 compares the two kinds of responses (hen eggs and quail eggs); the curve for quail eggs illustrates the essential aspects of graceful failure.



**Fig. 4** Load versus crosshead displacement for whole hen and blown quail eggs in compression between flat plates. Adapted from Ref 43

#### 3.2 Processing

The mineralization of eggshells seems analogous to that of marine shells, in that the organic material can influence the crystallization through its calcium-binding behavior. It was discovered in 1957 (Ref 37) that the matrix contains substances that have calcium-binding properties: acid mucopolysaccharide (especially chondroitin sulfate)/protein complexes. The idea then developed that the matrix plays an active role in the calcification process by binding calcium ions to itself, which then react with carbonate ions (produced by carbonic anhydrase in the oviduct) to form solid calcium carbonate (Ref 37). Such a mechanism would ensure that calcium carbonate is precipitated only in the eggshell and not in the lumen of the oviduct.

The binding of the calcium ions could promote growth by epitaxy or by causing a greater local supersaturation of that ion. Chelation is the most likely binding mechanism, since it would hold the ions in a precise steric configuration (Ref 38), and it has been shown that eggshell matrix can chelate calcium ions (Ref 39). It has also been suggested that where the mantles of the membrane fibers branch in the mammillary tips (the first regions of the shell to mineralize), they contain acid mucopolysaccharides with chelating properties that help in nucleation (Ref 40).

Various detailed compositions have been reported (Ref 23, 41, 42) for the organic matrix in different parts of the shell and also in different species. However, it appears that at least one calcium-chelating agent is present in all regions where mineralization occurs. Furthermore, an electron microscope study of eggshells at different stages of formation showed very clearly that the developing shell is always covered by a fine layer of organic matrix (Ref 40), which would be in keeping with a system in which the crystals develop on pre-existing organic material (Ref 39). See Ref 43 to 46 for reviews of biomineralization in avian eggshells.

geometry of the fibrous material, and researchers are only beginning to explore them.

## 4. Other Natural Substances

### 4.1 Wood

Owing to the historical use of wood as a structural material, the fact that it is a renewable resource, and its capability for graceful failure, structure-property relationships of wood have been studied in detail (Ref 2-4, 48). Softwoods can be viewed as a series of hollow tubes with walls consisting of helically wound fibers in a brittle polymeric matrix. (Hardwoods have a more complex structure.) This composite design provides a good combination of strength, toughness, and light weight.

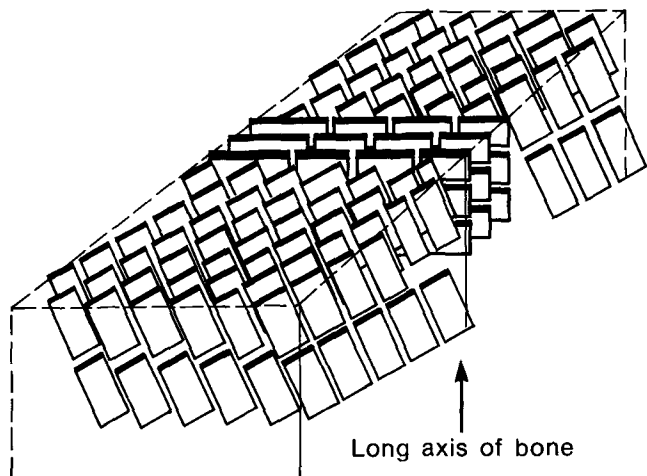
A novel fiber-reinforced composite based on this model was developed at the University of Bath, U.K. (Ref 49), and a patent was obtained (Ref 50). To date, it has not been commercially developed. Another variation on this theme was investigated at the University of Reading, U.K. (Ref 51). Both approaches mimicked the hollow, helically reinforced tubes with sheets of synthetic material (e.g., glass-fiber cloth) wound around a series of formers and impregnated with resin.

### 4.2 Bone

Although many investigations have been devoted to the study of bone, they have generally been motivated by biomedical applications, so for the most part this topic is not covered in this overview. It is noteworthy, however, that a new interpretation of bone structure in a rat tibia was recently advanced (Ref 52, 53). The crystals of calcium phosphate were determined to be aligned differently in alternate layers of protein fibers, in an arrangement described as "rotated plywood" (Fig. 5). Notice the similarity to the structure of Fig. 1d. The structure of rat bone represents an additional level of complexity over that of the pink conch shell in that the protein (principally collagen) is in fiber form, with the fiber axis of each lamella at an angle to the axes of its neighbors, and with the crystal faces in each lamella rotated around the fiber axis from one lamella to the next. Thus, the crystal layers of the thick lamellae are oblique to the lamella boundaries, whereas those of the thin lamellae are parallel to them.

This type of architecture hinders crack propagation and enhances toughness. Thus, an understanding of bone architecture could lead to the design of improved industrial materials. Studies are also underway to obtain a better understanding of the relationship between microstructure and toughness, both in highly mineralized bone and in less mineralized forms such as antler (Ref 54).

The mineralization of bone, like that of other calcareous structural materials of biological origin, is initiated by the formation of a collagenous network. This sequence can be loosely mimicked by precipitation of gypsum from liquid that contains gelatin both in solution and in a preformed extended structure. Accordingly, factors affecting the mineralization rate and the resultant microstructural development of mineral phase in the presence of organic material was studied with this model system (Ref 55). The necessary concentrations of calcium and sul-



**Fig. 5** Schematic illustration of the structure of rat bone, showing portions of two thick lamellae with a thin lamella sandwiched between them. Individual crystals, idealized as rectangles, are tens of nanometers long and wide; lamellae are on the order of microns thick. Source: Ref 53

### 3.3 Biomimesis of Avian Eggshells

In light of the functional success of eggshells as crack-resistant, protective packaging for embryo development in many biological species (Ref 43, 46), it is surprising that this model for structural biomimesis has been largely overlooked. One exception is an effort currently underway to develop a novel damage-resistant composite based on the design features of avian egg integuments (Ref 47). An essential aspect of avian eggshells is the intermittent attachment between the compliant, fibrous constituent (outer shell membrane) and the hard, brittle phase at the mammillary tips (Fig. 3). Detailed microscopic examination of eggshell fractures suggests that when growing microcracks reach the unattached regions, the load is "spread" over a much larger volume and rapid crack propagation is forestalled.

Experiments with composites (made up of a hard phase in domelike configuration, with fibers bonded to the dome tips) have resulted in graceful failures in bending, similar to those shown in Fig. 2, whereas conventional laminates of the same constituents failed catastrophically (simple, ramplike, load-deflection curves) (Ref 47). Many variations are possible for the

fate ions were obtained (and retained throughout the precipitation) by the addition of calcium sulfate hemihydrate ( $\text{CaSO}_4 \cdot 0.5\text{H}_2\text{O}$ ) to the gelatin solution. The hemihydrate was progressively hydrolyzed as the gypsum ( $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ ) was precipitated. The presence of gelatin altered the gypsum morphology to plates, compared to hexagonal rods in the absence of gelatin. However, the plates were randomly arranged, in contrast to the orderly arrays of hydroxyapatite plates seen in bone.

Three points should be kept in mind for consideration of biomimesis based on the structure of bone:

- The filler particles in bone are hydroxyapatite plates that are only about 4 nm thick. In contrast, the glass fibers in an epoxy composite, for example, are about 10  $\mu\text{m}$  in diameter.
- Bone plates are packed to high volume fractions, 40 vol% or more, owing to their parallel arrangements.
- Bonding between the apatite plates and collagen matrix in bone may be better than that between, for example, glass fibers and synthetic polymers.

### 4.3 Insect Cuticle

Insect cuticle is a composite structure of chitin fibers (composed of N-acetylglucosamine polymers) in a protein matrix. A wide range of properties is represented by cuticle, depending on the fiber content and on whether the protein is soft, or tanned (heavily cross-linked) and rigid (Ref 56). Cuticle consists generally of three layers: the outer layer is waxy and protects against water loss (the epicuticle); next is a rigid layer of fibers in a tanned matrix (the exocuticle); and the inner layer has a matrix that is untanned and soft (the endocuticle) (Ref 34). The detailed structure varies from species to species, but common features are a layered structure, in which fibril orientation varies helicoidally between layers, and a series of vertical channels (pore canals and gland ducts) that pass through the cuticle. The fibril arrangement around these channels prevents them from weakening the structure (Ref 57, 58). Cuticle provides the insect a casing of maximum stiffness and toughness for minimum weight.

Although cuticle and man-made composites are surprisingly similar in many respects, they differ in certain essential aspects of structure and organization (Ref 58-60):

- The plies in synthetic composites are of uniform thickness with multiple fibers distributed through the thickness of each ply, whereas each ply in insect cuticle consists of a single row of fibers and varies in thickness.
- Man-made fibers are generally of the same size and shape, but chitin fibers vary in size and geometry.
- The ply orientation of synthetic composites is symmetrical and balanced, while the orientation in insect cuticle is a dual helicoid, that is, asymmetrical and unbalanced.

### 4.4 Comparison of Natural and Synthetic Fiber-Reinforced Composites

Calvert (Ref 34) made an interesting comparison of mechanical properties between natural and synthetic fiber-reinforced composites, which is reproduced here as Table 2. The bony materials compare quite well against the filled polymers. Although the properties of insect cuticle appear unimpressive, the reliability of those measurements is in question, as Calvert pointed out, because testing of such small specimens is difficult.

## 5. Special Topics in Biomimetic Materials Processing

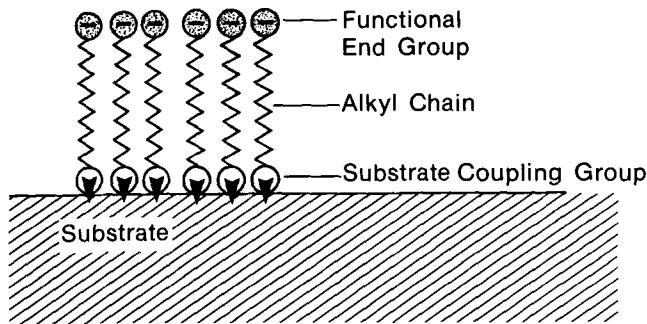
### 5.1 Thin Films

A topic of increasing importance in the mimicry of biomineralization processes is the fabrication of thin films. Thin films are essential constituents in various electronic, magnetic, and optical devices; abrasion- and corrosion-resistant protective coatings; sensors; catalysts; and ion-exchange devices. For example, there are identified needs for ceramic coatings on polymers, particularly for "active" coatings with special electronic, piezoelectric, or optical properties. Conventional processing (e.g., sintering) cannot be used without destroying the polymers. Even sol-gel methods require temperatures of at least 400 °C. An appealing alternative strategy is low-temperature aqueous processing, made possible through understanding and manipulation of interfacial chemistries, which can affect crystallization on specific substrates and control crystal orientation.

**Table 2 Properties of synthetic and biological composites**

Composite	Volume fraction of hard phase, %	Tensile modulus, GPa	Bend strength, MPa	Work of fracture, $\text{J/m}^2$
PEEK/AS4	61	140	2200	1900
ABS/short glass fibers	25	9.8	110	...
Sheet molding compound	...	10	130	...
Polybutylene terephthalate/glass beads	25	4.9	95	...
Insect cuticle	35	6-10	80	...
Enamel	92	45	76	200
Whale bulla	66	30	33	200
Dentine	48	12	250	550
Bone	41	16	270	1700
Antler	31	7.7	179	6200

Source: Ref 34



**Fig. 6** Idealized depiction of surface functionalization with a self-assembled monolayer, showing points of attachment to the substrate, self-assembled alkyl chains, and functional end groups to induce crystal nucleation and growth. Adapted from Ref 63

tations, grain size, and density. Such control elements are characteristic of biomineralization.

Recent work by Rieke et al. has demonstrated the efficacy of surface functionalization (via self-assembled monolayers, electrochemical deposition, or Langmuir-Blodgett films) and constant composition techniques to produce single-component ceramic films on polymers from aqueous solutions (Ref 20, 61-63). An example of surface functionalization with a self-assembled monolayer is illustrated schematically in Fig. 6. These studies have shown that the phase, crystal size, crystal shape, crystal orientation, density, and film location can be controlled by proper selection and modification of the substrate and solution. For example, deposition of iron oxide onto sulfonated polystyrene (to mimic a nucleation protein with its acid groups) produced films of high density, uniform orientation, and highly anisotropic habit of the crystallites. This processing route allows ceramic films to be grown in a one-step process and to be sufficiently dense so as not to need subsequent sintering. In contrast to gas-phase deposition, aqueous processing permits film formation on polymeric, amorphous, or mismatched substrates. It is also cheaper, simpler, and faster than gas-phase processes.

An approach that mimics both the physical and chemical control of biomineralization has synthesized and crystallized cadmium sulfide (CdS) within a polymeric matrix (Ref 64). Poly(ethylenoxide) (PEO) was used as the polymer matrix because it binds metal ions strongly, analogous to the organic matrix in biological systems. CdS was chosen as the mineral phase, in part because of its potential importance as a nonlinear optical material. Crystallites of CdS formed within the PEO film had regular cubic morphology, had rock salt structure (characteristic of the high-pressure phase of CdS), and were oriented with a-axes perpendicular to the plane of the PEO film. The process, however, was slow.

Another group has fabricated thin films of barium titanate ( $\text{BaTiO}_3$ ) (Ref 65) and titania/polymer composites (Ref 66) of interest for piezoelectric and electronic devices. Composites of poly (n-butylmethacrylate) and  $\text{BaTiO}_3$  were generated by in situ precipitation of  $\text{BaTiO}_3$ . Burnout of the polymer followed by firing produced fully dense ceramic thin films of  $\text{BaTiO}_3$  that had submicron grain size and were less than 20  $\mu\text{m}$  thick.

These films are much thinner than conventionally formed films with submicron grain size.

In summary, the lessons from biological systems suggest some significant advantages for the processing of thin films. Most important are aqueous, low-temperature processing and the ability to build composite, thin film structures out of materials not previously amenable to such processing, such as thin ceramic films on polymer substrates. Additional advantages and some remaining challenges to low-temperature biomimesis of ceramic thin films are:

#### Advantages

- Low-temperature, low-cost, environmentally benign processes
- Dense crystalline films without subsequent thermal treatment
- Uniform coating of complex shapes and porous materials
- Compatibility with polymers and other temperature-sensitive materials
- Microstructural control
- Direct deposition of patterned films with submicrometer-scale resolution

#### Challenges

- Supersaturation control for systems with extreme pH sensitivity
- Consumption of reagents during film formation
- Generation of unwanted metastable or amorphous phases
- Deposition of phases that require conditions too harsh for sensitive substrates (e.g., quartz, alumina)
- Low deposition rates
- Degradation of substrates in highly acidic or basic solutions
- Prediction of which functional groups will nucleate specific crystalline phases in specific orientations
- Control of solution conditions for multicomponent films

## 5.2 Self-Assembly

Self-assembly is the basis for all biological synthesis and processing. In the context of biomimesis, however, self-assembly (as opposed to self-replication) refers to the tendency of certain types of molecules to arrange themselves into specific arrays under suitable conditions. Examples of self-assembly in biological systems include the folding of polymers such as proteins, the assembly of proteins into higher organized structures such as membranes, the assembly of amphiphilic molecules into micelles, bilayers, and so on, and the larger-scale organization of organic and inorganic components into structural composites such as shells or bones (Ref 67). Most research in biomimetic self-assembly is directed at the biomimicry of membranes as a mechanism of organizing molecules into well-defined surfaces.

The basic building blocks of a wide range of biological membranes are lipids (fatty acids). These are long amphiphilic molecules (one water-soluble or hydrophilic end and one water-insoluble or hydrophobic end) that assemble themselves into aligned arrays, generally "tail-to-tail" bilayers with the hydrophilic head-groups in contact with the aqueous phases on either side of the membrane. Various types of self-assembling layers are known:

- *Planar BLMs* (bilayer lipid membranes) (Ref 68-70)

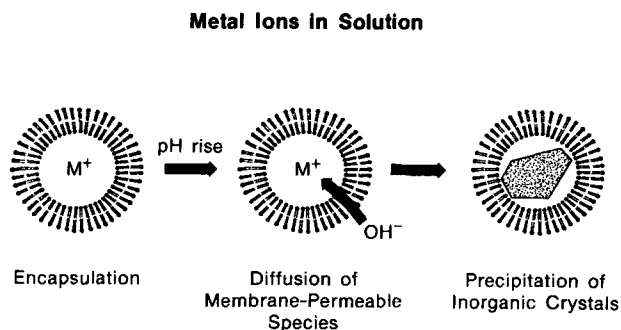


Fig. 7 Nanoscale synthesis of inorganic crystals in phospholipid vesicles. Adapted from Ref 76

**Table 3 Oriented nucleation of inorganic crystals under Langmuir-Blodgett monolayer**

Monolayer	[Metal]/mM	Mineral	Nucleated face
<b>CaCO<sub>3</sub> system</b>			
CH <sub>3</sub> (CH <sub>2</sub> ) <sub>16</sub> COO <sup>-</sup>	7-10	Calcite	(110)
	4-6	Vaterite	(001)
CH <sub>3</sub> (CH <sub>2</sub> ) <sub>17</sub> NH <sub>3</sub> <sup>+</sup>	4-10	Vaterite	{001} and (110)
CH <sub>3</sub> (CH <sub>2</sub> ) <sub>19</sub> OSO <sub>3</sub> <sup>-</sup>	10	Calcite	(001)
CH <sub>3</sub> (CH <sub>2</sub> ) <sub>19</sub> PO <sub>3</sub> <sup>2-</sup>	10	Vaterite	(001)
CH <sub>3</sub> (CH <sub>2</sub> ) <sub>17</sub> OH	4-10	Calcite and vaterite	Nonoriented and inhibited
C <sub>27</sub> H <sub>45</sub> OH(a)	4-10	Calcite	Nonoriented
<b>BaSO<sub>4</sub> system</b>			
CH <sub>3</sub> (CH <sub>2</sub> ) <sub>19</sub> OSO <sub>3</sub> <sup>-</sup>	0.15	Barytes	(100)
CH <sub>3</sub> (CH <sub>2</sub> ) <sub>19</sub> PO <sub>3</sub> <sup>2-</sup>	0.15	Barytes	(100)
		CH <sub>3</sub> (CH <sub>2</sub> ) <sub>19</sub> COO <sup>-</sup>	0.15 Barytes (010)
(a) cholesterol			

- *Vesicles* are BLMs that are quasi-spherical rather than planar. They separate an inner aqueous compartment from the bulk aqueous phase. It is possible to produce vesicles within vesicles, provided that they are separated by an aqueous phase (Ref 70-72).
- *Langmuir-Blodgett films*: Surfactants (amphiphilic molecules) form monolayers on the surface of an aqueous liquid. These monolayers can be removed intact from the surface, and they can also be "stacked" to form multilayers. These monolayers and multilayer assemblies are known as Langmuir-Blodgett films (Ref 70, 72-74).
- *Adsorbed monolayers* can be formed directly onto a solid substrate (Ref 72).
- *Monolayer lipid membranes (MLMs)* are aggregates of "bolaamphiphiles" or bipolar lipids. In other words, each molecule has two head-groups linked by a chain of hydrophobic groups. When the two head-groups are of different sizes, the molecules align themselves with smaller head-groups together and larger head-groups together, thus forming asymmetrical, curved membranes or vesicles (Ref 75).

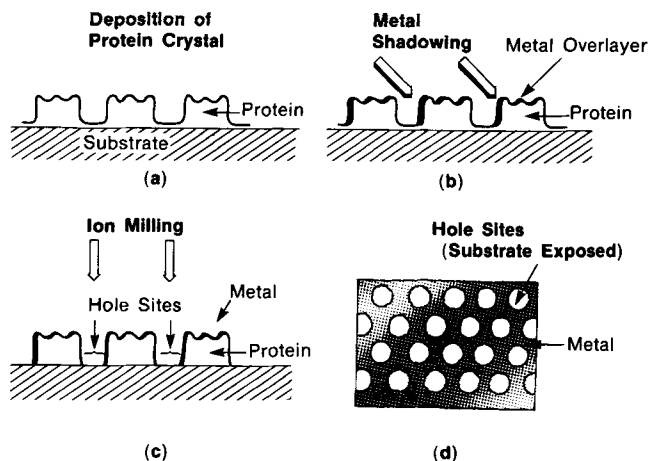


Fig. 8 Processing steps to make nanostructures by templating with proteins. (a) Deposition of protein crystals. (b) Shadow metallization of protein with titanium (1.2 nm). (c) Ion milling to remove metal from substrate. (d) Plan view of idealized nanostructure. Adapted from Ref 81

Some of these membrane systems have been studied for decades, and there are thousands of relevant papers in the literature. Of particular interest in our present context is the participation of self-assembly in mimicry of biomineralization. For example, both the phase (mineral type) and orientation of mineral nuclei can be controlled by appropriate choice of the Langmuir-Blodgett monolayer substrate and the solution concentration. The range of possibilities is suggested in the results presented in Table 3 (Ref 76).

In another study, self-assembled phospholipid vesicles were the reaction vessels for synthesis of ultrafine ceramic particles composed of yttrium, barium, copper, and silver (Ref 77). The vesicle membrane acted as a reaction cell for particle precipitation, an ion-selective membrane that affected precipitation kinetics, a barrier that prevented spontaneous agglomeration of the ultrafine particles, and a lubricant-dispersant that facilitated particle rearrangement during consolidation. A schematic representation of this approach is shown in Fig. 7. Such a process not only provided extraordinarily fine particles but also offered significant advantages in the mild processing conditions, particularly in contrast to traditional high-energy processing routes. However, precise control over chemical stoichiometry in multicomponent systems was found to be difficult.

Phospholipid vesicles have also served as reactors for the synthesis of nanometer-sized particles of cobalt ferrite (CoFe<sub>2</sub>O<sub>4</sub>) by aqueous-phase coprecipitation (Ref 78). These particles could have various commercial applications, such as recording and magnetic inks or feedstocks for sintered permanent magnets.

These results are exciting because they suggest that particles will someday be produced in finer sizes, leading to superior material properties. Further, the mild processing conditions offer the potential to make special compositions and structures that decompose at temperatures associated with conventional processing.



### 5.3 Nanostructure Fabrication

There is growing interest in the development of electronic, chemical, and/or optical devices with nanometer dimensions (Ref 79). Biological systems offer some options for achieving this important objective.

For example, although methods for deposition of metallic features with spacings on the order of 100 nm have been available for several years (Ref 80), recent work by Clark et al. has demonstrated that much finer-scale structures can be realized by templating with proteins (Ref 79, 81). Crystalline protein monolayers are attractive as templates for nanometer molecular lithography because their lattice parameters (5 to 30 nm) provide a periodic structure small enough to be useful but large enough to be readily characterized and manipulated.

The protein template chosen for the cited studies was the cell wall surface layer from *Sulfolobus acidocaldarius* bacteria, which is a porous monolayer, 10 nm thick, composed of protein dimers arranged in a two-dimensional triangular lattice with a 22 nm lattice parameter. The general process of templating with proteins consists of adsorbing a suitable protein on a substrate, metallizing the adsorbed protein, and argon milling the metallization to produce a geometric pattern (Ref 81), as illustrated in Fig. 8.

Clark et al. also explored the next step of the process, which is to functionalize the nanostructure by adsorbing active particles preferentially in the holes in the metal film (Ref 82, 83). Initial experiments were aimed at a biological adsorbate, ferritin, which is a proteinaceous shell surrounding an iron-hydroxide core. Other adsorbates for nanoheterostructures were tried subsequently, but good coverage was not obtained in any of the experiments.

## 6. Summary of Lessons from Natural Designs

The specific research cited above is a brief look at approaches that are being taken to develop materials inspired by natural designs. Following are some of the conclusions that are clear from the analysis of these efforts and other active investigations:

- Biological materials are complex composites, made up of very ordinary substances, that demonstrate superior mechanical properties such as stiffness, strength, and toughness. Man-made ceramics, for example, are notoriously brittle, whereas biological ceramics (teeth, marine shells) are not.
- The microstructures of biological materials provide multiple mechanisms for forestalling catastrophic failure, including crack deflection, crack branching, and energy adsorption by lath or fiber pullout.
- Lessons from the designs of biological materials include the hierarchical organization of the microstructures and the ways that living organisms achieve those structures.
- Various materials and structures found in nature have been characterized in detail, notably mollusc shells, avian eggshells, bone, and insect cuticle. Thus far, however, there have been only a few instances (MDF cement, biomimetic composites modeled on softwood or eggshell, laminar SiC/graphite) in which researchers have mimicked the mi-

crostructural design of biological systems with synthetic materials and obtained significant improvement in properties over those of materials with conventional microstructures.

- Research on the microstructures of mollusc shells has shown that natural ceramics with crossed-lamellar structure or brick-and-mortar structure have superior mechanical properties. Laboratory experiments to mimic those structures with synthetic materials (e.g., SiC and graphite) have resulted in improvements of about 400% on fracture toughness and more than 2000% on work of fracture over conventional SiC ceramics.
- The primary barrier to mimicking many natural material designs with man-made substances is the achievement of the elaborate hierarchical microstructures at the nanometer scale that are seen in biological materials. However, there is a developing capability for manipulation of nonbiological structures on this scale.
- An important consequence of research into natural material designs will be to enrich the imaginations of researchers about the relationships of microarchitecture to function.

## 7. Summary of Implications for Biomimetic Materials Processing

It is clear that opportunities exist to integrate biological processing methods with man-made materials to attain the goal of better materials. The following observations about materials processing seem central to future research directions:

- The nucleation and growth of biominerals are controlled in such a way that:
  - (a) The nucleation is induced in certain locations and prevented elsewhere.
  - (b) The phase of the mineral deposited on the substrate is determined.
  - (c) The size, shape, and orientation of the crystals are controlled.
- Biomimicry is attractive as a possible route to:
  - (a) Production of biomimetic composite architectures that would be inaccessible by conventional processing routes
  - (b) Improved control of crystal nucleation and growth (in nonbiomimetic structures)
  - (c) Inhibition of unwanted crystallization
- The mineral deposition process may be under direct cellular control, but it is more commonly controlled by a nucleation process. Nucleation proteins are water soluble and contain many negatively charged functional groups. They generally control crystal growth as well as nucleation.
- Current approaches to mimicry of crystal nucleation and growth control in biomineralization include:
  - (a) Mineral deposition onto polymers derivatized with functional groups such as sulfonates
  - (b) Mineral deposition onto suitably engineered Langmuir-Blodgett films
  - (c) Synthesis and crystallization of minerals with polymeric matrices that strongly bind metal ions
  - (d) Precipitation of minerals in polymeric matrices to serve as precursors to ceramic thin films. Subsequent poly-

mer burnout followed by sintering can produce fully dense films with submicron grain size, which are thinner than those obtainable by conventional processing.

- (e) Synthesis of nanometer-size ceramic particles in phospholipid vesicles
- Biomimetic fabrication of ceramic thin films from aqueous solutions has potential advantages over conventional processing: low-temperature, low-cost, and environmentally benign processes; uniform coating of complex shapes; and compatibility with polymers and other temperature-sensitive substrates.
- Templating with proteins, as a route to fabricating devices with features of nanometer dimensions, involves adsorption of a suitable protein on a substrate, metallizing the adsorbed protein, and argon milling the metallization to produce a geometric pattern for subsequent deposition or chemical reaction.

## 8. Concluding Remarks

A remarkable diversity of structures and molecular functions has evolved in animals and plants. Many of these natural substances have properties or capabilities that belie their origins in humble, everyday, starting materials. Consequently, there is a growing awareness among scientists and engineers that biological systems can be a valuable source of inspiration for man-made materials. It is hoped that this overview provides a useful introduction to the topic of biomimetic structures and processes and to the available literature.

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