

## Biomimetics

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**Abstract.** The well-organised multifunctional structures, systems and biogenic materials found in nature have attracted the interest of scientists working in many disciplines. The efforts have resulted in the development of a new and rapidly growing field of scientific effort called biomimetics. In this article we present a few natural materials and systems and explore how ideas from nature are being interpreted and modified to suit efforts aimed at designing better machines and synthesising newer materials.

**Keywords.** Biomimetics; biomineralisation; supramolecular chemistry; hierarchical structures.

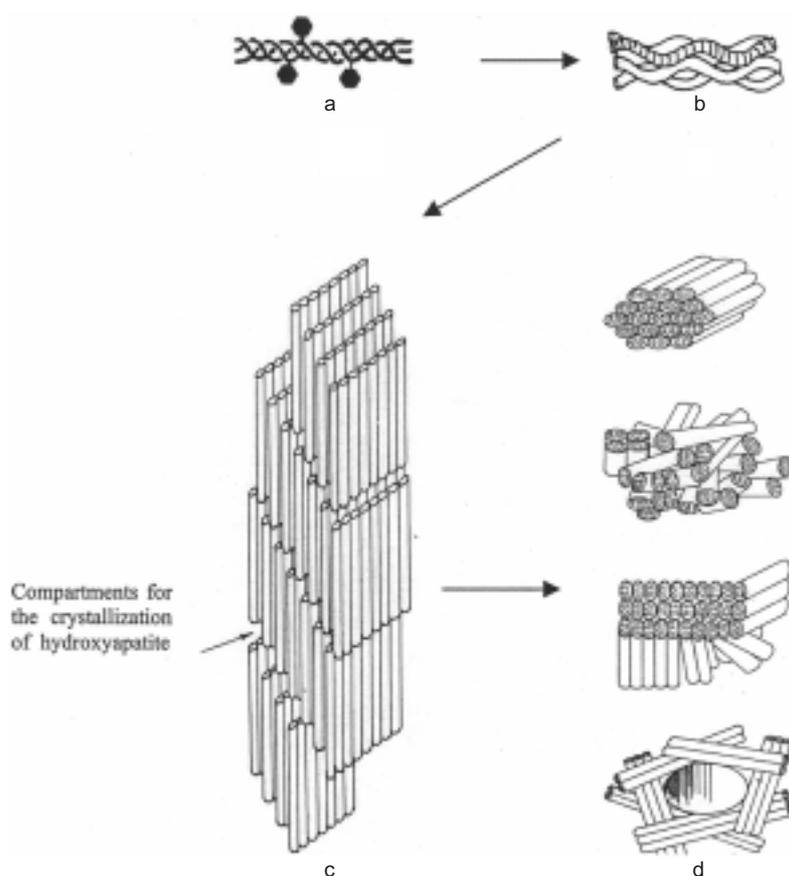
### 1. Introduction

Reverence for the beauty and usefulness of the naturally occurring materials around us has been felt and expressed ever since man learned to use them for improving the quality of life and standard of living. Various stages, in the growth of our civilization are therefore aptly named after stone, iron and bronze. It is customary to refer to the current millennium as the age of materials. This is no less a measure due to the rapid strides that the field of materials science and technology has made over the last fifty years or so. In our persistent attempts to improve the performance and versatility of a given material or combination of materials as in composites, we have learnt to observe and analyse the way nature has so successfully developed materials in living organisms and systems. Nature is yielding some of its long held secrets only now because of the increased sophistication and capabilities of the instruments of investigation that are at our disposal.

Nature uses very few materials to create a bewildering variety of life forms. Same material is used in many different ways to meet vastly different needs as exemplified by collagen. Natural materials are mostly constituted from organic, inorganic crystals and amorphous phases. The organic phase generally occupies a very small fraction of the total volume and has functions ranging from toughening the tissue to synthesising highly functional minerals. The inorganic components can be single crystals or aggregates of them arranged in well-ordered arrays to give a hierarchy of length scales. The interfaces between the soft organic matter and the relatively hard inorganic material is of paramount importance in determining the properties of the composite and nature has devised strategies for assuring integrity of the interfaces under demanding conditions of stress.

Natural materials are self-generating, hierarchical, multifunctional, nonlinear, composite, adaptive, self-repairing and biodegradable. Bones in animals illustrate some of these charac-

teristics. The constitution and structure of the bone differs from animal to animal and even within the same animal from place to place in order to serve the specific needs. At the molecular level bone consists of collagen and hydroxyapatite crystals. Three strands of the collagen molecule are wound to form a tropocollagen molecule. Such molecules are arranged in a staggered fashion to overlap and leave spaces at each end of the molecule. A sequence of such molecules forms a microfibril. These microfibrils form large fibrils. The collagen fibrils in turn form layers. These layers or lamellae then organise into a variety of assemblies (see figure 1). Bone is both load bearing (e.g. the femur) and protective (e.g. the skull). Bone serves a metabolic function also being a store for calcium, phosphorous and other ions. It can repair itself and exhibit several physical properties such as piezoelectricity (Anderson & Ericksson 1970) and pyro-electricity (Lang 1966). In spite of a lack of complete understanding of the way bone senses the load on it, it is well established that it has an adaptive capability. Bones slowly add or lose mass and change their form in response to modifications from normal stresses. When subjected to sustained cyclic loading *in vivo* it densifies and thickens with an increase in mass. On being subjected to continuously lower than normal stresses, it thins and



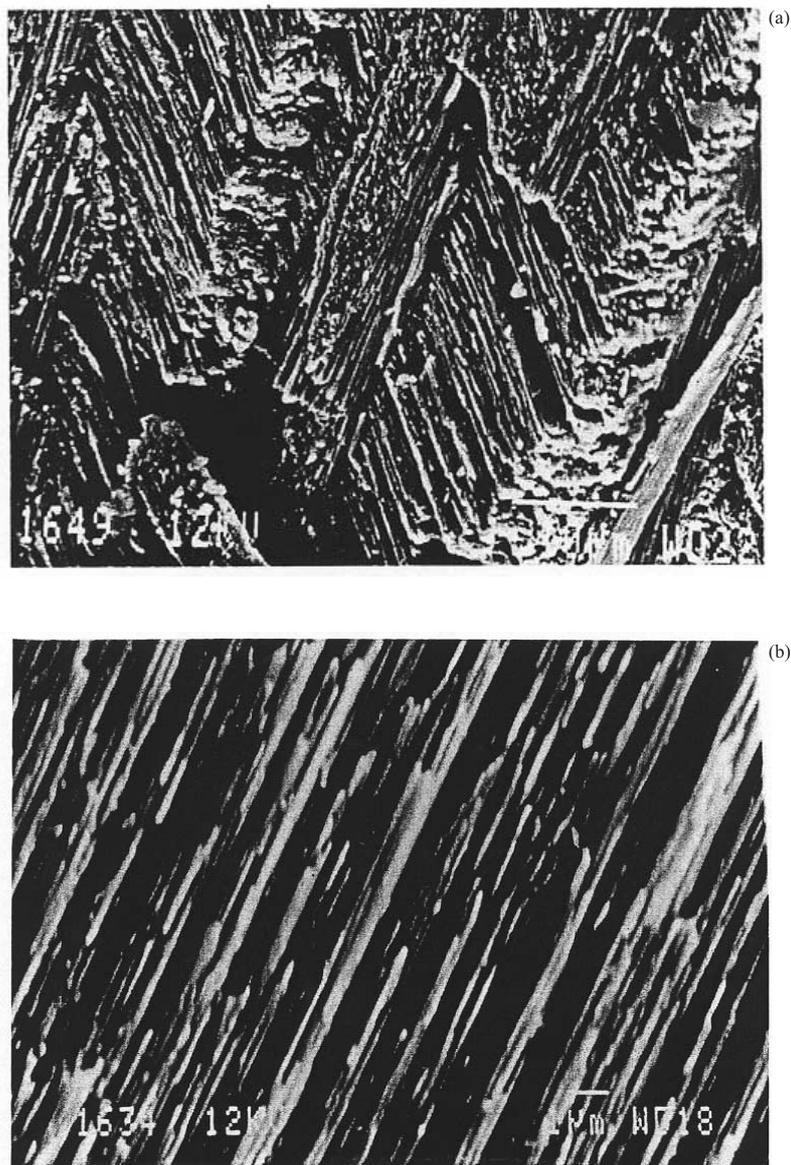
**Figure 1.** Organization of collagen framework: (a) collagen triple helix, (b) bundle of collagen triple helix, (c) assembly of collagen fibrils and (d) crystallisation of hydroxyapatite particles in collagen fibrils and their possible self-arrangements leading to bone formation.

reduces in density and weight. This phenomenon is indicative of the ability of bone to adapt itself to the changing demands of the sustained stress levels to which it is subjected (Lakes 1993). In this respect bone is a smart material even if the response time is longer.

Biogenic inorganic crystals exhibit stunningly different properties from their corresponding synthetic counter parts. This has led to the questioning of the assumption that biogenic and inorganic crystals are intrinsically the same (Berman *et al* 1993). For example, silica in the sponge  $\{(SiO_2)_3 \cdot H_2O\}$  monorhaphis is found in the form of a spicule of up to 3.0 m length. In the cross section, it is composed of several concentric layers varying in thickness from 10  $\mu\text{m}$  in the centre to 3  $\mu\text{m}$  at the periphery. The layers are deposited on an axial organic fibre. Under three-point bend testing, it exhibits strength of 593 MPa as against a value of 155 MPa for synthetic silica. The work to fracture is also 30 times higher in the spicule (Levi *et al* 1989). Intercalation of acidic macromolecules into the crystal lattice appears to be common. Similarly, spider dragline silk is far superior to steel of comparable dimensions and the energy to fracture on equivalent weight basis is 100 times higher (Vincent 2001). The shell of the mollusc abalone, made of essentially calcium carbonate (see figure 2a), has 3000 times greater fracture resistance than the single crystal of calcite (Jackson *et al* 1988; Currey 1977). Such examples together with increasing pressure towards the conservation of the environment have led materials scientists and engineers to carefully study natural systems, their design and their methods for the synthesis of constituent materials. In the present article, we provide some examples of the way nature builds tissues and synthesises materials and review the attempts being made to use such strategies for learning to design systems and develop novel materials.

## 2. Biomimetics: Definition and scope

Biomimetics is the field of scientific endeavour, which attempts to design systems and synthesise materials through biomimicry. Biomeaning life and mimesis meaning imitation are derived from Greek. Perceptions regarding the scope of biomimetics appear to vary very widely depending upon the specialized discipline of the investigator. Japanese electronic companies are supporting biomimetic research with a view to learning the way biological systems process information. Recent interest of Japanese in biomimetic research seems to arise from the health and welfare problems of an ageing society leading to studies on the development of human supportive robots (ATIP 1999). Biomedical engineers consider biomimetics as a means of conducting tissue engineering and trace the origins of biomimetics to ancient times when Mayan, Roman and Chinese civilizations had learnt to use dental implants made of natural materials. Material scientists view biomimetics as a tool for learning to synthesise materials under ambient conditions and with least pollution to the environment. Chemists have always wondered at the ease with which ammonia is produced in biological nitrogen fixation, methanol is produced in biological oxidation of methane and oxygen is generated in photosynthesis (Shilov 1996). They hope to learn the synthesis of polymers that can perform the roles of enzymes in such processes. Biologists study biomimetics not only for an understanding of the biological processes but also to trace the evolution of various classes of organisms. Biochemists have interest in the field due to the complexities associated with the interaction of biopolymers with ions of metals leading to the mineralization in living organisms. Even geologists have an interest in biomimetics because of biomineralization: the formation of extra- or intra-cellular inorganic compounds through the mediation of the living organism. Engineers attempt to explore the relationship between structure and function in natural systems with a view to achieve analogous synthetic design and manufacture. On the



**Figure 2.** (a) The crossed lamellar structure of an abalone shell. (b) Co-aligned aragonite rods in mollusc shell.

whole, the field of biomimetics addresses more than one issue. Those engaged in this field of research activity try to mimic natural methods of manufacture of chemicals in order to create new ones (imitate barnacles for producing a natural glue), learn new principles from phenomena observed in nature (flight of birds and insects, swimming of fish and aquatic animals), reproduce mechanisms found in nature and copy the principles of synthesising materials under ambient conditions and with easily available raw materials.

Even though biomimetics literally means to mimic biology, Vincent (1997) has argued that it is far more difficult to exactly mimic a living system for engineering purposes than to understand the underlying ideas and principles for designing systems of use. He argues that the farther we are from the natural the more powerful will be the concepts developed and greater the chances of transferring the technology from nature to engineering (Vincent 1997). It has also been suggested that blindly copying nature may not be advisable. In this article we shall address only two aspects of design of structures and biomineralization in natural systems.

### 3. Designs from nature

Designs found in nature are the result of millions of years of competition for survival. The models that failed are fossils. Those that survived are the success stories (Benyus 1997). Consequently they are optimised for economy of energy consumption and use of space Mattheick (1994). Nature makes economic use of materials by optimising the design of the entire structure or system to meet multiple needs. For example, feathers besides helping the bird fly insulate it from the environment. The many ways in which nature tries to design a system to suit a function is best illustrated with respect to fish. Fish reduce the drag as they swim both through chemical and structural devices. Some of them release substances, which make their skin slippery. In others, the body is designed to aid avoidance of turbulent flow around it during swimming. In some fish gill slits are formed and located on the body such that smooth flow of water around the fish is ensured. In sharks, skin scales possess tiny ridges that run parallel to the longitudinal body axis and reduce the drag (Dickinson 1999). In porpoises, the skin is designed and made to absorb pressure fluctuations thus preventing turbulence. The cuttlefish has a buoyancy tank with a number of chambers, which are filled with nitrogen or water to facilitate energy efficient movement from one depth to another. The structure of the buoyancy tank is such as to resist external pressures of the order of 7 atm (Birchall & Thomas 1983).

Attempts to adopt designs based on the study of plants and animals have a long history. Oft quoted examples are the attempts of Leonardo da Vinci to design an aircraft based on his study of birds, the design of the Crystal Palace, London, and of the Eiffel Tower, Paris (Meadows 1999). The Palace design was based on the observation of the structure, unusual size and great strength of the leaves of a water lily called *Victoria amazonica*. Joseph Paxton, a gardener by profession, was fascinated by the intricate ribs and cross ribs at the back of the leaf of this lily and built a greenhouse the roof of which incorporated a similar scaffold. He later entered the design in a competition organised for architects called to design an exhibition hall for arts and industrial goods. When completed the Crystal Palace was 108 ft in height and covered an area of 18 acres. It stood the test of time from 1851 to 1936 before a fire destroyed it. Similarly, the origins of the design of the Eiffel Tower are traced to the inspiration derived from the structure of the head of the femur in the thigh. Hermann Von Meyer, professor of anatomy at Zurich observed that the head of the femur has many fingers of bone arranged in curving lines. The Swedish engineer Karl Cullman recognised the engineering importance of the arrangement and noted that they coincide with the lines of stress experienced by the bone. He showed that the femur and its structure is the best way of transferring the off-centre forces of the hip to the long bones of the leg. Gustaff Eiffel, the French structural engineer implemented such principles in building the now well-known landmark of Paris.

Among the more recent examples of designs drawing inspiration from nature may be mentioned the invention of the fabric fastener Velcro<sup>®</sup> and the paints based on the behaviour

of water on the lotus. George de Mestral, a Belgian, noticed that the cocklebur from burdock plant stuck tenaciously to the fur of his rather big dog when it ran through grass during their walks. On microscopic examination, he discovered that the burrs had tiny hooks. He translated the natural design into commercial practice by combining a part with hooks and a surface with a felt to create the now common fabric fastener (Meadows 1999). Makers of a newly patented paint have derived their inspiration from the age-old observation that water does not stick to lotus leaves. It has been found that the lotus leaf has tiny wax-coated protuberances on its surface. These new paints clean themselves after every rain (Dickinson 1999). Further, Paul Sperry noticed, in 1935, that while he slipped on snow, his dog did not. On examination of the dog's paw, he found deep wave-like grooves. This simple observation enabled him to launch Sperry Top-Sider Shoes with similar grooves for safe walking in winter (Meadows 1999). Many more such examples can be cited from daily life. Today the defence funding agencies of the advanced countries are spending considerable sums of money to evolve designs of robots based on living things like fish, geckos, aquatic birds with webbed feet, bees, butterflies and a host of others.

#### 4. Biomineralization

Nature employs more than 60 inorganic materials together with organic matter to create myriads of organisms. In the bones of vertebrates, the most common mineral phase is carbonated apatite and the organic part is collagen fibril. Members of phylum Echinodermata have calcite that contains magnesium and is distributed in protein matrix. The shells of molluscs (snails, slugs, clams, oysters, cuttlefish, squid etc.) contain aragonite (see figure 2b). Amongst different plants, silica is more commonly observed. It is also found in some marine organisms such as radiolaria, sponges and the marine plants; diatoms (Weiner *et al* 2000). Other inorganic phases found are mostly of calcium oxalate, gypsum, barite and a few iron oxides.

Even nanocrystals of metals are found in living organisms in their native state. Klaus *et al* (1999) have found that a silver-resistant microorganism called *Pseudomonas stutzeri* AG 259 can accumulate silver in the form of 200 nm sized crystals embedded in its organic matrix. The weight of silver accumulated could be as high as 25% of the biomass. The silver crystals form in the space between the outer membrane and the plasma membrane and have been shown to be in mostly elemental form. Some evidence was also provided for the crystallization of silver sulphide and another as yet undetermined silver-bearing structure. Other examples include the formation of tellurium in *Escherichia coli* K12, enzymatic reduction of technitium and the production of selenium by several organisms (Klauss-Joerger *et al* 2001).

Magnetosomes, the magnetite crystals produced by magnetotactic bacteria ( $\alpha$ -proteobacteria) in the intracellular space, best illustrate the functionality of minerals produced through biomineralization. These crystals have size specificity (with most of them falling within 35 to 120 nm along the long axis) and distinctive morphology. The size enables uniform magnetisation of the crystallite with a single domain being operative. The particles are arranged such that their crystallographic axes of easy magnetisation align themselves. These characteristics are ideally suited for magnetotaxis in the earth's magnetic field (Moskowitz 1995). Another very recent finding is the detection of 100  $\mu\text{m}$  dia. crystals of ilmenite in the combs of the hornet *vespa orientalis* by Stokcroos *et al* (2001). These magnetically polydomain crystals are said to act like spirit levels and aid the hornets to assess the symmetry and balance of the cells they are building. Whether these crystals are collected by the hornets or synthesised by them is unknown. However, the presence of the titanium and iron in the body of the hornet cannot rule out the possibility of synthesis *in situ*.

The composition of the crystals produced is also tailored to suit specific requirements. Some times, it varies along the length of even a single crystal. The calcite prisms found in the tooth of a sea urchin provide the best example. The magnesium carbonate concentration in the calcite varies from about 4.5% at one end to about 13% at the other. The chemical composition is also specific to the taxa (Wang *et al* 1997). There has been a debate if the biogenic inorganic phases are identical to the synthetic crystals. Evidence now available suggests that the biogenic crystals are different in the sense that they have considerable intercalation of acidic macromolecules derived from the proteins (Berman *et al* 1993).

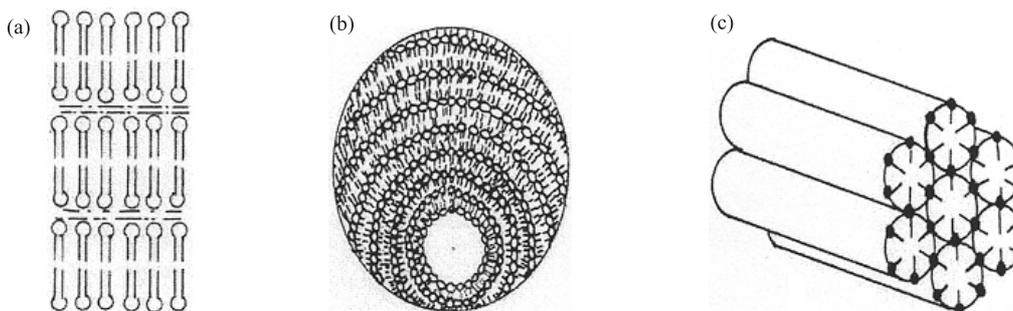
Biomineralization occurs under ambient and mild conditions. Biomineralization could be extra-cellular or within the cell (or organism). The production of magnetite by iron reducing bacterium *Geobacter metallireducens* (GS-15) is an example of biologically induced mineralization. The bacterium produces magnetite by coupling the oxidation of organic matter to the reduction of ferric ion (Moskowitz 1995). In extra-cellular crystallisation, the cell or organism may affect the solute concentrations in the medium and provide sites for nucleation and growth. The secretion of biopolymers like collagen and chitin into the crystallisation domain enables the construction of large-scale structures such as bone and shell. The growth of such large structures through extra-cellular nucleation requires control of both the biopolymer and crystal deposition at large distances by the cells. Usually growth occurs by the movement of a mineralization front. Cells on this front control the nucleation process while growth takes place in the regions behind the front (Calvert 1992).

Biomineralization within the organisms has attracted the attention of both biologists and material scientists in view of its importance both in understanding species diversity and evolution as also the mechanisms of formation and functional characteristics of the mineral produced. In this case, the crystals form in the vesicles, surrounded by a membrane. The size, shape, composition and crystallographic orientation of the mineral produced are controlled very closely. Formations of calcite in coccoliths, magnetite particles in *A. magnetotacticum*, etc. are examples.

Biomimetic approaches based on an understanding of the biomineralization process are aimed at synthesising nanoparticles, polymer mineral composites and templated crystals (Mann 1993; Mann *et al* 1993; Sinha *et al* 2001a). Studies over the last few years show that there are several distinct characteristics of biomineralization.

- (a) Biomineralization occurs in well-constructed compartments or microenvironments.
- (b) These compartments have the ability to promote the nucleation and growth of crystals of the required inorganic material at chosen sites while effectively preventing the formation of other crystals.
- (c) The crystal size and shape are well defined and show little variation, if any.
- (d) Formation of the macroscopic structure is through the packaging of many such units. The structures that arise are highly organised from molecular (1–100 Å) to macro-scales through nanometric (10–100 nm) and mesoscopic (1–100 μm) domains. These are hierarchical in nature and meet the functional requirements.

The substrate on which mineralization occurs is composed of proteins, glycoproteins, lipids or polysaccharides (see figure 3). In some cases, it may just provide a passive support. Often, the substrate provides both stereo chemical basis and physiosorption for nucleation and growth of the mineral (Sarıkaya 1999). The biological macromolecules of the substrate also collect and transport the material required for mineralization. The organic matrix also controls the shape and orientation of the resultant crystal (Vincent 2001). Some of the matrix material



**Figure 3.** Hierarchical structures formed by lipids and surfactants containing a hydrophilic head and a hydrophobic tail. (a) bi-layer, (b) vesicle and (c) hexagonal array.

gets occluded into the crystal and can determine fracture behaviour of the crystal (Berman *et al* 1988). A number of studies have shown that some of the proteins have the ability to even determine the structure of the crystal. For example, specific proteins are responsible for the formation of amorphous calcite (Beniash *et al* 1997), silica and calcium phosphate (see Stupp & Braun 1997). When proteins extracted from mollusc shells, which are either made up of calcite or aragonite, are added to the system in which crystallisation of either of these phases is taking place they change the phase being crystallised. Proteins extracted from aragonite bearing shells help nucleate aragonite while those extracted from calcite containing shells nucleate calcite (Falini *et al* 1996). In abalone, the outer portion of the shell contains calcite while the inner portion contains aragonite. Recent atomic force microscopic studies have shown that the transition from calcite to aragonite during crystallisation from a solution can be induced by the addition of soluble proteins extracted from the abalone shell nacre without the need for a pre-formed matrix (Thompson *et al* 2000).

Many of the proteins have both soluble and insoluble parts. In the mollusc shell, for example, two types of proteins are found on the basis of its solubility in ethylene diamine tetra acetic acid (EDTA). Proteins rich in aspartic acid and glutamic acid with some covalently bound sulphated polysaccharide content and proteins with serine and a large fraction of sulphated polysaccharides are soluble portion of the organic matrix. Proteins rich in glycine, alanine, phenylalanine and tyrosine are insoluble in EDTA. It is believed that the insoluble part provides nucleation sites. Such parts of the protein contain a high concentration of carboxylate groups such as glutamic and aspartic acid residues, which enable interaction between, organic chain and mineral ions like  $\text{Ca}^{2+}$ . Weiner has suggested that amino acid sequences of the type Asp-X-Asp (where the 'X' stands for a neutral residue) are good binding sites for calcium (Weiner 1984). The soluble part is generally highly anionic and their role is to restrict nucleation to specific sites by inhibiting nucleation in the bulk. There are also a number of examples where the polymer from the protein gets entrapped in the growing crystal thereby controlling the shape of the crystal (Berman *et al* 1988).

#### 4.1 *Microstructure resulting from mineralisation*

The properties of natural materials arise in a large measure due to the ordered spatial structures that exist over many length scales. We find a bewildering variety of microstructures arising from biomineralization. The grain size, shape, boundaries and the crystallographic texture vary greatly. The microstructure of mollusc shells is the most studied and molluscs are considered as the "master builders" (Addadi & Weiner 1997). At least seven different types of

microstructures have been observed (Chateigner *et al* 2000; Vincent 2001). These are: (i) Prismatic both simple and spherulitic; (ii) nacreous both columnar and sheet; (iii) gross-lamellar, both simple and complex; (iv) homogeneous.

The simple prismatic microstructure consists of mutually adjacent prisms while the spherulitic prismatic structure consists of coarse first-order prisms with second-order prisms originating from spherulitic sectors at the surface. In the columnar nacreous structure columns of uniform-sized tablets are formed. The sheet nacreous structure has a typical brick wall pattern. The crossed lamellar structure consists of parallel laths or rods with two non-horizontal dip directions of their elongated sub-units in adjacent lamellae (see figure 2a). This structure is layered at five distinct length scales and can be considered to be a ceramic “plywood” (Kuhn-Spearing *et al* 1996). This is the most common amongst molluscs and often it is the only type of microstructure in a given shell occupying both its inner and outer layers. The anisotropy associated with this microstructure has the ability to deflect cracks and offer resistance to their propagation resulting in the enhancement of toughness of the shell. The homogeneous microstructure has equiaxed irregularly shaped crystallites. By virtue of the way the inorganic component is built into the organic matrix, some of these microstructures can be expected to exhibit very strong texture in x-ray diffraction patterns. Experiments have shown that it is indeed so in case of nacreous structures where a close correspondence has been found between texture and microstructure (see figures 2a, 2b). In other cases, even similar looking microstructures may exhibit different x-ray textures and vice versa (Chateigner *et al* 2000).

#### 4.2 Evolution of the microstructure

Some very elegant and relatively recent experiments, using atomic force microscope coupled with the newly developed scanning conductance microscope, have shown that the nacreous microstructure consisting of bricks of calcite and mortar of polysaccharide and protein fibres arises in a rather unexpected way. The cell first constructs the organic matrix and then induces crystallisation of the inorganic material. Layers of polysaccharide and protein are laid down orthogonal to each other with the sheets parallel to the aragonite crystal base having a number of holes. It is postulated that these holes both supply the necessary raw material for the growth of the crystal and maintain the alignment (see Addadi & Weiner 1997). Prior to these studies, it was thought that the crystals form first and are subsequently enveloped by the organic material. Similar studies on other morphologies should help in elucidating the mechanisms of their formation.

Brown *et al* (2000) have recently developed a genetic system in the bacterium *Escherichia coli* to study protein-mediated control of crystal growth and used crystallization of gold as a model. They isolated the polypeptides that control the morphology of gold crystals and discovered that they act catalytically by an acid mechanism. They were able to create a controlled assembly of nanometre-scale gold particles on selected surfaces in aqueous solutions.

### 5. Bio-composites

As seen from the previous section, many of the tissues in living organisms are bio-composites consisting of the soft organic material and the hard mineral. Calvert (1992) has classified bio-composites into four types on the basis the interplay between of interactions at the mineral-matrix interface. In type I composites (Chiton teeth, algae) the matrix is inert and does not

possess specific nucleation sites. Growth of the crystals is spatially restricted. Consequently, there is no control of the matrix on crystal size, orientation and morphology and it acts as a support encouraging heterogeneous nucleation of the inorganic phase. In type II composites (Avian egg shells, limpet teeth) the matrix offers specific sites for nucleation and controls crystal orientation and may encourage a polymorph preferentially. Size and shape of the crystal are not still subject to control by the matrix. In type III composites, the matrix inhibits nucleation of the crystals. The structure, size and morphology of the inorganic phase are also matrix controlled. Amorphous inorganic phases form. In type IV composites, site directed and regiospecific nucleation occurs with regulation of the growth, structure, morphology and orientation of the inorganic crystals. Bone, mollusc shell are examples of this type.

The most striking feature of the biocomposites is that the organic matrix occupies barely 3 to 5% of the volume but imparts considerable improvement in the mechanical properties of the mineral. Thus, nacre, which is the lustrous inner layer in the mollusc shell, has 500 to 3000 times greater toughness than chalk, which constitutes 95% of its bulk. Detailed studies have shown that propagation of cracks is impeded in various ways thus contributing to the enhancement in fracture toughness. It is not possible to achieve similar fracture toughness in synthetic composites. One of the reasons for our inability to fabricate composites similar to the bio-composites lies in the glues that are employed. Synthetic composites use either epoxy or silicon adhesives. The former are stiff while the later are elastic. The energy involved in breaking both is inadequate to impart necessary fracture toughness. Nature finds a unique way of improving the fracture toughness as has been shown recently in studies conducted on abalone shells. The natural proteins in the shell provide a modular fibre in which different domains are held together with intermediate strength bonds as compared to the bonding within the molecule. On increasing the stress and before molecule's backbone can break, the modules unfold and begin to yield. Such events occur repeatedly in long molecules that are compacted into number of domains. The work required for fracture is thus enhanced considerably (Smith *et al* 1999).

### 5.1 Structure-*junction relationships in bio-composites*

Tissues in living organisms have specific roles to perform. These composite tissues are specifically designed to meet well-defined needs. The example of the tooth of the sea urchin illustrates this concept very well (Wang *et al* 1997). The tooth has three main parts; (i) the plate zone, (ii) the keel, and (iii) the stone part. The sea urchin uses the stone part of the tooth to scrape algae from hard rock surfaces for its food. The stone part should therefore have very high hardness compared to the other two parts. It has nearly twice the hardness of the plate and about 1.5 times the hardness of the keel. In order to achieve the necessary hardness calcareous needles are connected to primary plates of calcite by lamellae or finer plates. The keel zone is mostly constituted by calcite prisms and has an outer layer of secondary plates. The plate zone consists of plates of calcite which lie parallel to each other but at an oblique angle to the long axis of the tooth shaft. The primary plates that give single crystal diffraction patterns have a central core of amorphous calcite. Thin discs fill the space between the primary plates. The keel and the stone parts form fibre-reinforced composites in which the discs of calcite act as the matrix and the calcite prisms are the fibres. The S-shaped fibre stretching from the base of the keel to the tip of the stone exhibits both differences in shape and composition along its length. It has a diameter of only 1  $\mu\text{m}$  in the stone part with 4.5 mol% of  $\text{MgCO}_3$  and about 20  $\mu\text{m}$  dia. with about 13 mol% of  $\text{MgCO}_3$  at the end of the keel. As a result, the ratio of the volume % of fibres to discs varies from 50:50 in the stone part to 90:10 in the keel. This

intricate design and microstructure enables the sea urchin's tooth to provide the necessary hardness and strength to scrape the rocks for its food as well as the ability to sharpen itself.

Another example of nature's composite is bamboo, which has the ability to withstand high velocity winds. On a macroscopic scale the nodes, which occur periodically along the length of the bamboo, impart stability and rigidity to the plant. The cleavage and tensile strengths across the fibre direction are also raised considerably in the presence of the nodes. An analysis of the stresses experienced by the bamboo during bending indicates that the maximum stresses are generated at the outer part of the culm. The microstructure of the bamboo indicates that the density of distribution of the vascular bundles, which act as the reinforcing component, is the highest in the outer green layer. The fibre structure of the bundle also changes as one approaches the inner layers. Further the winding of the bast fibres in the vascular bundles is complex and consist of several alternate thick and thin layers. The microfibrils in each layer are distributed in a helical way with different elevation angles for the thick and thin layers when measured with respect to the fibre axis. These angles change gradually to avoid discontinuities between different layers. Bamboo is thus a functionally graded material and a hierarchically designed composite (Amada 1995). In contrast, synthetic fibre reinforced composites have far simpler and homogeneous distribution of the fibre in the matrix. When attempts were made to copy the bamboo structure, it was found that the strength of the synthetic composite could be doubled for the same ratio of graphite and epoxy resin composites. Industrial production is still difficult due to the intricacies of the winding machines that will be required for the distribution of the filament (Zhou 1994).

## 6. Optimised design: Lessons from nature

Observations and studies made on trees, teeth and bone reveal the following aspects of their design.

- (a) Biological structural members optimise themselves to maintain uniform stress across the cross section
- (b) Both trees and bones add material in the overloaded areas to compensate for the stress increase
- (c) Bone also has the ability to resorb material from under-loaded regions
- (d) They are self-annealing and self maintaining as in the case of sea-urchin.

Computer-aided optimisation of design by the Kernforschungszentrum, Karlsruhe (Mattheick 1994) used these principles. The group developed three methodologies named: Computer Aided Optimisation (CAO), Soft Kill Option (SKO) and Computer Aided Internal Optimisation (CAIO). CAO was able to provide simple optimization procedures for the modification of a design without concentration of stresses but failed to indicate the portions where there is no need to have material. SKO was developed to address this specific shortcoming of CAO. CAO and SKO are used alternately to arrive at the most optimised design. They provide an optimised solution for the outer shapes with the axiom of constant stress. As mentioned earlier the finger-like internal structure of the femur in a human body arises to provide strength along the lines of stress. CAIO attempts to provide the optimal distribution of fibres in a composite arranged to come c with the force flow in the component. It ensures, by such an alignment, that shear stress between the fibres does not arise. Mattheick (1994) also considered the ethical issues involved in optimising the design on the basis of lessons from trees and bone since the failure rates in biological structures are known to be a result of inadequate safety factors.

Another interesting case of learning to design through lessons from nature pertains to the development of a tuna like robot. Evolution over millions of years have made the fish a truly capable swimming machine (Triantafyllou & Triantafyllou 1995). Some of the characteristic features of fish are: the ability to accelerate very fast (pike can reach accelerations of 20G), low turning radius of only about 10–30% of its body length (achieved without loss in speed), high velocity (about 40 knots in case of yellowfin tuna) and the conservation of energy during a dive to lower levels. As early as 1936, the ability of a dolphin to swim at speeds of up to 20 knots was considered a paradox due to the seemingly small weight of the fish. Triantafyllou & Triantafyllou (1995) have found that the thrust-inducing vortices generated by the flapping of the tail of the fish are at the centre of the efficiency of swimming of these aquatic creatures. The tail of a fish pushes the water backwards and creates a column of moving fluid called a 'jet'. The jet includes the vortices and derives its propulsive efficiency. The process of swimming can be analysed in terms of Strouhal number, defined as the product of the frequency of swishing of the tail and the width of the jet divided by the speed of the fish. For most fish the value of this number is around 0.3. Triantafyllou & Triantafyllou (1995) observed that the efficiency reaches values of about 86% when the Strouhal number is in the range 0.25–0.35. In contrast propeller driven underwater ships reach an efficiency of only 40%. Recent studies by this group have indicated that it is the body of the fish, rather than the tail, that creates the strongest vortices (Daviss 2000). Based on these observations a swimming machine with a flapping tail has been constructed and submarines and boats with a flapping tail are likely to be seen soon.

Zhou (1994) reported the design of an ideal interface for carbon reinforced metal-matrix composites. The design was based on the study of interfaces in natural materials, which exhibit excellent physical and chemical Compatibility and possess gradient changes of structure and composition. For the carbon fibre reinforced titanium alloys, a pyrolytic carbon (PC)/TiC or TiN/Ti interface was found to be suitable while a PC/SiC/Si or PC/AlN/Al combination was found to be good for aluminium based composites containing carbon fibres.

Similar benefits have been derived in the design of aircraft by a study of birds and insects (Wootton 1990).

## 7. Biomimetic synthesis

Lack of complete understanding of all the steps involved in biosynthesis prevents us from exactly mimicking Nature to produce highly monodisperse, ordered and hierarchical structures. For example, it is still not possible to produce the drag net silk of the spider even with the knowledge of its molecular constitution. As pointed out by Calvert (1992), three possibilities exist for the synthesis of materials by mimicking biological systems. These are (i) direct use of organisms for the synthesis (ii) use wholly synthetic methods and (iii) use some modification of the biological processing technique. Attempts made along these lines by various investigators will now be reviewed.

### 7.1 Use of organisms

Genetically engineered bacteria are now being employed to produce proteins that can be drawn into fibres. Genetic engineering involves the snipping open of the double helical strands of the DNA molecule and replacing the nucleotide-coding units with others, which may have been produced by synthetic methods. Such a procedure involves the production of a synthetic DNA by sequential addition of nucleotides to a chain anchored on a solid support. The synthesised

sequence is then multiplied by a polymerase chain reaction. Such units are then joined end to end with the aid of suitable enzymes to produce a synthetic gene. The artificial gene is introduced into the plasmid of the bacterial cell using appropriate enzymes for snipping open the DNA of the plasmid and inserting the new sequence. On returning the plasmid to the cell, the cellular mechanism uses the new sequence of the DNA to synthesize proteins that have been targeted. This procedure is suited for the synthesis of elastin and silk-like materials (Ball 1996).

Dameron *et al* (1989) have discovered that the yeasts *Candida glabrata* and *Schizosaccharomyces pombe* synthesize highly monodisperse CdS particles when cultured in the presence of cadmium salts. The crystallites made by the organisms have structures that are somewhat different from the synthetic crystals. The crystals in *S-pombe* have shorter Cd–S bonds and the structure is that of rock salt. This structure is stabilised in synthetic CdS only under high pressure. The *C. glabrata* complex gives crystals with a structure that is intermediate to the equilibrium zinc-blende type and rock salt-type. Such nanocrystalline semiconductor particles have great importance because of their quantum behaviour and tunable optical absorption and photosynthetic properties.

As pointed out already, the process of biomineralisation takes place in compartments created by the biopolymers. Use of biological molecules and their synthetic counterparts is therefore an appropriate strategy for biomimicry. Meldrum *et al* (1991) attempted and succeeded in synthesising nanocrystalline materials with the use of ferritin cages. Ferritin is an iron-storage protein in which the peptide subunits are assembled into a hollow sphere of 8–9 nm. Internal diameter. They employed three different approaches to the synthesis: (a) *in situ* chemical reaction of native iron oxide in the core with chemicals that can pass through the peptide-based membrane, (b) redox reactions involving metal ion uptake and deposition of empty protein cages (apoprotein) and (c) ion binding and hydrolytic polymerisation of metal ions within the apoferritin cages. Using these strategies they have successfully synthesised manganese and uranium oxo-species inside the protein cavities. We have also demonstrated that the nanosized cavities present in globular proteins can be used as nanosized reactors for the synthesis of monodispersed inorganic particles such as cadmium sulfide (Nayar *et al* 2001).

Mendelson (1992) has succeeded in producing fibres with the aid of bacteria (*Bacillus subtilis*). When the bacterium is cultured in media containing metal salts, the cell wall of the bacterium aids in biomineralisation and incorporates the metal ions in the product, which can be drawn into fibres. The cell walls behave as complex ion exchangers and their capabilities are comparable to commercial ion exchangers. The product is known as bionite. Product of biomineralisation in the presence of iron and copper can also be incinerated to yield magnetite particles or metal crystals of small dimensions.

## 7.2 Synthetic methods

Almqvist *et al* (1999) have tried to produce materials with the structure of nacre by the use of physical methods of processing. The aim of the study was to keep the composition of a polymer–talc composite as close to that of nacre made of biopolymer–CaCO<sub>3</sub> combination and to orient the talc tablets in the desired fashion. They studied the suitability of seven different fabrication methods such as centrifugation, sedimentation, dipping, spinning and shearing. Their efforts could not reproduce the high degree of ordering, interfacial bonding between the organic and inorganic phases, low organic content and the ability to arrest or deviate the cracks as in nacre. Consequently, the mechanical properties also suffered. The only notable success was with respect to achievement of significant talc tablet orientation in the synthetic composite.

Rhee & Tanaka (2001) have used a novel precipitation and consolidation method to produce a hydroxyapatite/collagen/chondroitin sulphate nanocomposite that partly mimicked the composition of cartilage. They used calcium hydroxide suspension and phosphoric acid solutions with varying concentrations of collagen and chondroitin sulphate. The precipitates were shaped and consolidated via filter pressing and cold isostatic pressing respectively. They found a texture in the alignment of hydroxyapatite crystals. The *c*-axis of the nanocrystals was aligned along the longitudinal direction of the collagen and chondroitin sulphate mixture.

In another study, Sellinger *et al* (1998) have successfully synthesised nano-laminated coatings that attempt to mimic the structure of nacre. They start with a homogeneous solution of soluble silicates, coupling agents, surfactant and organic monomers and initiators prepared in an ethanol-water solvent. They dip a polished (100)-silicon substrate into the solution and then withdraw and irradiate it with ultraviolet light to initiate organic polymerisation. As the coating dries, evaporation of ethanol enriches the concentration of other constituents (particularly surfactant and water) resulting in micelle formation and their assembly along with appropriate distribution of the inorganic and organic precursors. The coatings were featureless at micrometre length scale but showed well-ordered alternate layers of organic and inorganic material of nanometre dimensions on electron microscopic observation. The composites formed were poly (dodecylmethacrylate)/silica, poly (4-methylstyrene)/silica and poly (4-vinylbenzylchloride)/silica.

Recently Cha *et al* (2000) have synthesised a series of block copolypeptides of cysteine-lysine that have the ability to mimic silicatein (a protein found in the silica spicules of the sponge *Tethya aurantia*). The synthesised block copolymers provide the first example of polymers, which can hydrolyse and condense an inorganic phase (tetraethoxysilane) and also provide a template in the process. They were able to produce hard mesoporous silica spheres and assemblies of columnar amorphous silica. Cha *et al* (2000) determined the specific conditions under which the columnar structures were stabilised and also elucidated the mechanisms involved in hydrolysis and condensation of the inorganic phase. The studies have attracted attention since the inorganic phase was produced from tetraethoxysilane under ambient conditions at a neutral pH. Similarly many investigators are using synthetic body fluid to obtain nanocrystalline materials. The work of Tas (2000) is an example. In this study, nanocrystalline calcium hydroxyapatite (50 nm) was precipitated after dissolving calcium nitrate tetrahydrate and diammonium hydrogen phosphate in synthetic body fluid at 37°C and pH of 7.4 and adopting a novel precipitation technique. The resultant crystals of hydroxyapatite were found to be stable even up to 1600°C in air.

### 7.3 Imitation through self-organisation

An important aspect of biological tissues is that they are formed by the self-organisation of biopolymers and enzymes under cellular control. Three-dimensional folding of polymers produces a hierarchical structure from the nanometre to macro scale levels and the cavities and surfaces generated are fruitfully employed for the nucleation and growth of inorganic phases to construct the tissue with the desired functional properties (see figure 3). It has therefore been the endeavour of several investigators to produce hierarchical structures by exploiting several physical and chemical principles. Many disciplines of science are coming together to create organised hierarchical structures that are comparable to those observed in biological systems. Supramolecular chemistry, which has developed rapidly over the last decade or so is concerned with the manipulation of directed interactions in order to design structures. Its initial interest was in the mimicking of biological systems through synthetic routes (Desiraju 2001). The soft matter community studies the principles underlying self-assembly and tries

to interpret the phenomenon in terms of statistical-mechanics. Molecular biology attempts to manipulate the genetic apparatus to understand the biological pathways to organisation. Some of the attempts made through such synergic interaction are briefly discussed in this section.

Self-organisation is a property of a number of familiar materials such as liquid crystals, block copolymers and hydrogen bonded complexes, soaps, lipids etc. The interaction is brought about through hydrophobic and hydrophilic effects, Coulomb and Van der Waals forces. Muthukumar *et al* (1997) have discussed the theoretical basis for self-organisation and identified that three guiding principles offer means of exploring different length scales in self-organising structures. These are; (i) the existence of competing interactions and sequences, (ii) entropic frustration and topological dereliction, and (iii) spontaneous selection of primary length scales. They also discuss ways and means of achieving self-organisation in synthetic materials. Simultaneously, with such studies number of experimental investigations has also been reported in the literature. Examples of these will now be discussed.

Thurn-Albrecht *et al* (2000) used diblock copolymers composed of polystyrene (71 vol%) and polymethylmethacrylate to arrays of 14-nm-dia PMMA cylinders hexagonally packed in the PS matrix with a lattice constant of 24 nm. These arrays could also be oriented under an electric field when annealed above the glass transition temperature of both the constituents. After removal of the minor component, a nanoporous film is formed. Thurn-Albrecht *et al* electrodeposited metal in the pores to form nanowires to yield densities in excess of  $1.9 \times 10^{11}$  wires/cm<sup>2</sup>. Wires formed from ferromagnetic materials have superior properties.

Kresge *et al* (1992) have successfully synthesised molecular sieves with channel dimensions in the range of 16 to 100 Å or more through the calcinations of aluminium silicate gels in the presence of surfactants. In the first step hexagonal arrays of cylindrical nacelles were formed with the polar groups of surfactants being on the outside. Silicate species introduced in the form of tetra methyl ammonium silicate solution and precipitated silica occupy the spaces between the cylinders. It was argued that either the anionic alumino-silicate species enter the spaces between surfactant cylinders to balance the cationic hydrophilic surfaces of the micelles or are themselves responsible for the formation of the hexagonal arrays. Autoclaving the mixture at 150° for 48 hours eliminates the organic matter and leaves hollow cylinders of inorganic materials arranged in the form of a sieve.

Another way of creating a reaction chamber similar to those found in natural systems is to employ amphiphiles or molecules that have a polar "head" attached to a nonpolar alkyl chain. Such molecules self-organise due to the hydrophilic nature of the head and the hydrophobic nature of the tails. The molecules are capable of self-organisation and form ordered structures in one (lamellar), two (hexagonal) and three (cubic) dimensions. Of these, vesicles are spherical or elliptical closed bilayer membranes in the size range of 200–5000 Å. One can also produce bicontinuous rods with three-dimensional periodicity. These can undergo topological transformations on heating or cooling (Funari & Rapp 1999). Lipids are the most commonly used substances due to the presence of the hydrophilic polar or bipolar group and two long hydrocarbon chains that are hydrophobic. Natural egg lecithin and synthetic compounds such as hexadecylhexa (oxyethylene glycol) ether (C<sub>16</sub>EO<sub>6</sub>), dipalmitoyl-DL- $\alpha$ -phosphatidylcholine, dimiristoil-DL- $\alpha$ -phosphatidylcholine are the commonly used materials. Vesicles are formed by the injection of an ethanol solution of lipid into water or by the ultrasonic treatment of lipid suspension in water. They have a water pool inside and required chemical can be dissolved in this water. Vesicles are

characterised by a large membrane surface ( $1 \text{ m}^2/\text{ml}$ ). Phospholipid unilamellar vesicles of about  $300 \text{ \AA}$  diameter have been used by Mann *et al* (1986) to synthesise iron oxides. They found that the size, shape and structure of the precipitates formed in the vesicles differed from those produced by precipitation in aqueous solutions. Ion transport and binding, shape and size of vesicles etc. were found to influence the precipitation process inside the vesicle. The possibility of producing tube-like or disk-like composites containing minerals has been explored by Archibald & Mann (1993) with the use of a sugar-based lipid galactocerebroside.

Velev *et al* (2000) have shown that aqueous droplets suspended in fluorinated oil can act as reaction chambers and template highly ordered and smooth particle assemblies. Aqueous droplets of colloidal suspension were first placed on the surface of a perfluoromethyldecalin, which is immiscible with water and is dense. The droplets contained various concentrations of negatively charged polystyrene latex microspheres of  $270\text{--}300 \text{ nm}$  diameter.

The assembly is capable of self-organisation. As the water from the droplets was driven out by desiccation, the droplets shrank in size and ordered structures were formed inside them. The shape of the suspended template droplets could be controlled by interplay of interfacial tensions (which can be changed through the addition of surfactants), gravitational forces, latex concentrations and droplet sizes. Incorporating more than one type of particles in the drops could form complex composites. The method promises to be very useful for the synthesis of assemblies of oxides, semimetals etc.

#### 7.4 Crystallisation on patterned organic substrates

Another way of controlling nucleation of desirable crystalline phases is the generation of monolayers of a variety of materials through self-organisation or through deposition of organic polymers, inorganic polymers and biomolecules. The monolayers can present a range of functional groups at which nucleation can be initiated. Mann *et al* (1988) demonstrated that stearic acid monolayers could assist in controlled crystallisation of  $\text{CaCO}_3$  from supersaturated solutions. Crystallisation in the absence of the monolayer gave rhombohedral calcite while that nucleated by stearic acid had the structure of vaterite with the (001) planes of the crystallite being parallel to the organic substrate surface. Mann *et al* (1998) also observed that the degree of compression of the monolayer was important for achieving a degree of homogeneity and explained the observation in terms of electrostatic and stereochemical interaction between the inorganic phase and the organic matrix.

With reference to the formation of CdS particles in yeast, Biaconi *et al* (1991) found that the process can be mimicked by the use of poly (ethyleneoxide). They exploited the observation that this polymer binds metal ions very strongly. A glass slide was immersed first in an aqueous solution containing the polymer and  $\text{CdCl}_2$ . The film formed on it was then immersed in a solution of tetrahydrofuran containing  $\text{S}(\text{Si}(\text{CH}_3)_3)_2$ . CdS was found to form after 10 days of reaction. The organic polymer matrix was considered to mediate in the synthetic inorganic reaction and control the morphology of the particles.

In our studies, we have selected polyvinyl alcohol gels to form patterned organic substrates (Sinha *et al* 2001b). The polymer was dissolved in doubly deionised water at  $90^\circ\text{C}$  to yield solutions with the concentration of the polymer being in the range 2% to 10%. In one set of experiments polymer solutions of known concentrations were separately mixed with equal volumes of 0.5 molar calcium chloride solutions. The solutions were vigorously stirred for 30 minutes and a 0.1 molar solution of sodium carbonate was slowly added. It reacts with the calcium chloride already present in solution to yield calcium carbonate.

The system was let undisturbed for up to 20 days during which the colour of the solution turned milky white indicating that crystallisation has occurred extensively. In another set of experiments, the PVA–CaCl<sub>2</sub> solution was slowly heated and held at 70°C for an hour and cooled. This resulted in the formation of a dry gel, which was soaked with 0.1 molar sodium carbonate solutions for 48 hours. After washing the resultant mass with distilled water and acetone it was dried. In all cases, the morphology of the resultant crystals was examined under a scanning electron microscope. It was found that the 2% PVA–CaCl<sub>2</sub> solution produced spherulites of calcite having fine radiating crystallites emanating from a central nucleation site. This morphology closely resembles the aragonite spherulites of regenerated snail shells of *P. Paludosa*. Oriented and elongated calcite crystals were formed in the organic matrix containing 4% PVA. Such structures are identical to those observed in *renilla reinformis*. Almost periodically placed layers of calcium carbonate with disc like morphology were produced in the 6% PVA–CaCl<sub>2</sub> dried gel. The morphology resembled the nacreous growth of *P. Martensi lamellae*. These interesting results show that it is possible to obtain many of the morphologies of calcite observed in living organisms with the aid of a single polymer by controlling the concentration and treatment. Further studies are in progress.

### 7.5 Use of microemulsions

If extended architectures in three dimensions are to be mineralised to obtain some degree of hierarchical synthesis, one can utilise bicontinuous reverse microemulsions (Walsh *et al* 1994). In their study, crystallisation of calcium phosphate in nanoscale-interconnecting rod-like water conduits of bicontinuous water filled microemulsions was facilitated. The microemulsions were produced from mixtures of a surfactant and metastable aqueous solutions of calcium phosphate. While the resultant materials represented replicas of the microemulsion architecture, the pore sizes were incommensurate suggesting that modifications to the microstructure occur during crystal growth. In a recent study Chan *et al* (1999) produced three dimensional ceramic nanostructured films from *m*-silicon containing triblock copolymer (type A<sub>1</sub>BA<sub>2</sub> with polyisoprene as A and poly(pentamethyldisilylstyrene as B) films exhibiting double gyroid and inverse double gyroid morphologies. The ceramic nanostructure obtained by them possessed three-dimensional periodicities, which are not accessible to lithographic techniques. The ceramic also exhibited high temperature chemical and dimensional stability and can have uses as a membrane at high temperatures.

## 8. Technological uses of products of biomimetic synthesis

Current interest of many branches of science ranging from electronics to molecular biology is the manufacturing of complex, heterogeneous structures of well-controlled architecture and function. Even though the field of biomimetics is still in its infancy some tangible applications are on the horizon. The British biotechnology company Zeneca, a subsidiary of ICI, manufactures a biodegradable polymer Biopol which is produced by the bacterium *Alcaligenes eutrophus*. The polymer, which is similar to polypropylene, is used to produce moulded items such as bottles and for controlled release of drugs (Ball 1996). The extremely high-density nanowires have the capability of acting as high-density storage media when formed from cobalt due to enhanced coercivity and ferromagnetic properties. The young discipline of biomimetics has already proved that it is capable of contributing to sustainable technologies. If the characteristic features of natural synthesis such as energy and raw

material consumption efficiency, use of readily available materials, multifunctionality etc., are further copied and developed synthetically, we shall see a change in manufacturing strategies and greater movement towards sustainable development.

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