HIERARCHICAL STRUCTURES IN BIOLOGY AS A GUIDE FOR NEW MATERIALS TECHNOLOGY

NATIONAL MATERIALS ADVISORY BOARD

COMMISSION ON ENGINEERING AND TECHNICAL SYSTEMS

NATIONAL RESEARCH COUNCIL

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COMMITTEE ON SYNTHETIC HIERARCHICAL STRUCTURES

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Cover photograph: Scanning electron micrograph of the fracture surface of the wing cover of a Bessbeetle (Popilius disjunctus). Courtesy of Steve Gunderson, University of Dayton Research Institute.

Cover diagram: Structural hierarchy of cellulose in wood. Courtesy of D. Kaplan, U. S. Army.

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ABSTRACT

Hierarchical structures are assemblages of molecular units or their aggregates that are embedded or intertwined with other phases, which in turn are similarly organized at increasing size levels. The multilevel architectures are capable of conferring unique properties to the structure. Hierarchical structures are found in practically all complex systems, particularly naturally occurring ones. Synthetic hierarchical structures can be prepared from metals, ceramics, or polymers, or from hybrids of various classes of these materials.

The Committee on Synthetic Hierarchical Structures made an assessment of the opportunities to prepare hierarchical structures that possess useful and unusual physical properties for civilian and military applications. It conducted case-studies by selecting natural material systems to be used as models for synthetic efforts. It reviewed the state of the art of synthetic techniques and processes for assembling synthetic hierarchical structures. The committee also characterized properties, unusual characteristics, and potential end-use applications for these synthetic systems. Finally, the committee recommended research directions to expedite the understanding of the complex phenomena involved, lead to increased coordination among disciplines, and provide direction for future activities in the field.

PREFACE

Many materials systems found in nature exhibit a combination of properties that is not found in synthetic systems. The unique performance of natural materials arises from precise hierarchical organization over a large range of length scales. These materials display unique properties that are affected by structure and generative processes at all levels of the biological structural hierarchy.

At the request of the Department of Defense and the National Aeronautics and Space Administration, the National Materials Advisory Board convened a committee, the Committee on Synthetic Hierarchical Structures, to review techniques related to the preparation of hierarchical structures that possess useful and unusual physical properties and assess the opportunities for these structures in civilian and military applications. Although a broad range of functions are represented in biological systems, the committee concentrated on structural material systems.

The approach taken by the committee was to conduct case-studies that selected natural material systems to be used as models for synthetic efforts; characterize properties, unusual characteristics, and potential end-use applications for these synthetic systems; review state-of-the-art synthetic techniques and processes for assembling synthetic hierarchical structures; and recommend research that will expedite the understanding of the complex phenomena involved, lead to increased coordination among disciplines, and provide direction for future activities in the field.

In Chapter 1, the concept of hierarchical materials systems is introduced. Chapter 2 examines hierarchical architecture and illustrates its significance through a discussion of the structures and properties of a variety of biological materials systems. Several examples of synthetic hierarchical materials systems are described in

Chapter 3. Chapter 4 assesses the current capacity to produce such materials. And Chapter 5 presents the conclusions and recommendations of the committee, identifies areas of science and technology where hierarchical materials systems could play important roles, and suggests the research objectives that must be met to realize the potential of this new approach to materials technology.

David A. Tirrell
Chair

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HIERARCHICAL STRUCTURES IN BIOLOGY AS A GUIDE FOR NEW MATERIALS TECHNOLOGY

EXECUTIVE SUMMARY

Great fleas have little fleas,
upon their backs to bite 'em,
and little fleas have lesser fleas,
and so on infinitum,
and the great fleas themselves,
in turn, have greater fleas to go on,
While these again have greater still,
and greater still, and so on.

William DeMorgan (1839–1917)

Hierarchical structures are assemblages of molecular units or their aggregates that are embedded or intertwined with other phases, which in turn are similarly organized at increasing size levels. Such multilevel architectures are capable of conferring unique properties to the structure. Hierarchical structures can be prepared from metals, ceramics, or polymers, or from hybrids of various classes of these materials. The unifying theme for all types of materials is the pervasiveness of hierarchical structures in practically all complex systems, particularly naturally occurring ones.

Many materials systems found in nature exhibit combinations of properties not currently found in synthetic systems. The unique performance of natural materials arises from precise hierarchical organization over a large range of length scales. The hierarchical architectures of cellulose aggregates in wood or collagen aggregates in cartilage or tendon provide excellent examples of natural composite

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materials designed for multifunctional applications. Even the ultrasoft membranes surrounding cells exhibit exceptional properties that emanate from structure on many length scales. Studies of materials of biological origin invariably yield surprises that demonstrate clearly that these properties have been refined by slow evolutionary engineering. These hierarchically structured materials display unique properties that are affected by structure and generative processes at all levels of the biological structural hierarchy.

Hierarchical materials systems in biology are characterized by:

- recurrent use of molecular constituents (e.g. collagen), such that widely variable properties are attained from apparently similar elementary units;
- controlled orientation of structural elements;
- durable interfaces between hard and soft materials;
- sensitivity to—and critical dependence on—the presence of water;
- properties that vary in response to performance requirements;
- fatigue resistance and resiliency;
- controlled and often complex shapes, and
- capacity for self-repair.

Nature has a very limited range of materials with which it works. In most biological tissues, the constituents are proteinaceous. In rigid composites, they tend to be calcium carbonates, calcium phosphates, and silica. While natural composites exhibit outstanding combinations of properties, these materials systems and their constituent components exhibit the properties over a temperature range too narrow for most engineering designs. Thus, although rules about adhesion, architecture, and composite elements in mechanical collaboration are useful to learn from nature and to apply to other material components in order to produce analogous synthetic structures, the natural constituents themselves have performance deficiencies. It is the unique interfaces in natural composites that provide unusual mechanical performance in such materials.

Although the use of synthetic hierarchical concepts is at an early stage, the range of materials is potentially great. In addition, many structural variables can be altered more readily in synthetic materials than in natural materials. Through control of fabrication processes, materials variables such as atomic structure; molecular structure; nanostructures and boundaries; dislocation and other defect structures; cells and other substructures; size, distribution, and morphology of constituents and phases; grain size and morphology; orientation distributions; phase relations (including transformations); interfaces at all levels; and microstructure can be altered (although, for the most part, not independently). However, the realization of the potential of synthetic hierarchical structures has been limited, because available processing technology does not provide methods for precise control of materials variables over all levels of structural arrangement.

When synthetic materials are manufactured with an emphasis on tailoring their properties through microstructural control, the extent of this control is generally at a specific length scale. For instance, the mechanical properties of most metallic materials are controlled through the manipulation of dislocation dynamics at the nanometer length scale, whereas the mechanical properties of ceramic materials are controlled through the propagation of cracks that are initiated from defects of micrometer length scales. For composites that are composed of two constituents, which are generally of quite different character, the controls are much more complex.

At the request of the Department of Defense and the National Aeronautics and Space Administration, the National Materials Advisory Board convened the Committee on Synthetic Hierarchical Structures to conduct case-studies by selecting natural material systems to be used as models for synthetic efforts; review state-of-the-art synthetic techniques and processes for assembling synthetic hierarchical structures; characterize properties, unusual characteristics, and potential end-use applications for these synthetic systems; and recommend research that will expedite the understanding of the complex phenomena involved, lead to increased coordination among disciplines, and provide direction for future activities in the field. Although a broad range of functions are represented in biological

systems, the committee concentrated on structural materials systems and their properties.

CONCLUSIONS AND RECOMMENDATIONS

Biological structures are characterized by hierarchical architectural designs in which organization is controlled on length scales ranging from the molecular to the macroscopic. These materials are multifunctional and are produced in situ at room temperature and atmospheric pressure, although at slow rates. Many such structures are self-healing and remarkably durable, and many display properties that change in response to a changing environment; features that represent desirable, and as yet unattainable, objectives in the design and manufacture of synthetic materials systems. Nature is parsimonious in its use of constituent materials; it returns to the same materials again and again to realize an astonishing range of structure and function.

The hierarchical architectures of biological materials systems rely on critical interfaces that link structural elements of disparate scale. The study of such systems reveals extraordinary combinations of performance properties, as well as limitations due to the modest thermal and chemical stabilities of biological molecules. Application of hierarchical design concepts to more-robust synthetic building blocks provides promising routes to high performance adhesives and composites, biomedical materials, highly specific membrane and filtration systems, low friction bearings, and wear-resistant joints.

Biological structures are fabricated via highly coupled, often concurrent, synthesis and assembly. Although these assembly processes provide valuable lessons for synthetic processing, they generally occur at rates that are too slow to be economically viable. However, in the conception and evaluation of synthetic and processing schemes for new materials systems, the prospects for integrated system fabrication should be carefully considered.

The prospects for new biologically inspired materials technologies are real, however, full exploitation of this approach will

require advances in engineering, education, and enabling science. Although there is a broad range of technologies that may contribute to the understanding of biomaterials, the committee recommends concentration on developments in structural biology, interface science, synthetic methods for polymers with controlled sequences and r ethods for producing patterned structures by localized chemical synthesis, instrumentation, modeling, and theory (in materials, chemistry, biology, mechanics, etc.) to enhance the development and applications of hierarchical systems that are based on natural analogies.

Biological structures perform as parts of integrated systems and undergo continuous evaluation and refinement based on system performance. In analogous fashion, considerations of integrated systems design and performance will take on increasing importance in the high-technology materials-related industries of the future. Interdisciplinary teams of scientists and engineers will be required to effectively design and develop structural systems with such complex architectures. The committee recommends that the academic and industrial sectors of the materials community prepare for this development through implementation of appropriate educational and engineering programs that are based on systems concepts.

SCIENTIFIC OPPORTUNITIES

Examples of hierarchical structures in synthetic materials range from those that are deliberately biomimetic (e.g., ultrathin layered composites) to those whose relation to natural systems is coincidental (e.g., highly oriented polymers). The utility of many synthetic hierarchical materials is currently limited by the availability of fabrication technology, excessive fabrication times, and high cost for finished parts. This is especially true for very high performance materials, that is, continuous fiber reinforced composites materials (polymer, ceramic, metal-matrix, etc.) designated for use under environmental extremes, or parts which must function reliably for extended time periods. Similarly, there is always a need for more-efficient and more-sophisticated system designs, from improved

performance aircraft and spacecraft to faster-switching communication devices. The scientific and technological opportunities identified below represent examples of areas in which biological hierarchical paradigms may be effectively utilized to satisfy societal needs and solve existing problems.

Synthetic Methodology

The design and preparation of hierarchical materials will place a new premium on the synthesis of macromolecules of precisely defined primary structure and complex chemical composition. At present, the only methodology available for the preparation of such polymers involves the use of gene synthesis and recombinant DNA-technology to create artificial structural proteins. This methodology is powerful and may lead not only to the creation of polymeric materials with functions not obtainable through conventional synthetic methods but also to an understanding of how control of molecular structure and function can impact improved materials performance. It is clear, however, that the thermal and hydrolytic sensitivities of proteinaceous materials will limit their usefulness in many important synthetic materials applications. Generalization of the methods of controlled synthesis to new classes of monomers thus becomes an important objective.

Looking beyond templated polymerization, there is little current evidence of real progress toward efficient synthesis of genuinely uniform polymer chain populations. Nevertheless, recent advances in living ionic and metathesis polymerization have been substantial and may in time lead to higher-order control of chain length, sequence, and stereochemistry. The committee believes that issues such as environmental impact of the manufacture and disposal of polymers and the need for continuing improvement of cost/performance within the polymer industry will cause polymer science to move in directions that will tend to minimize the numbers of monomers (raw materials) utilized by the industry and hence reduce the number and volume of the offending chemicals presently in the waste stream. To achieve

this, while preserving or expanding the current product diversity available with commercial polymers, increased interest in the effects of specificity of the primary structure of synthetic polymers on cost and performance will be manifest.

Cellular Synthesis of Materials

Biological cells can be employed to fabricate thin layers (of organic materials or minerals) on synthetic material substrates. The objective is to employ organisms to structure materials on difficult-to-manage length scales and with difficult-to-synthesize chemistries. The cellular mechanism is capable of organizing fibrous networks, for instance, with functional hydrogel components to produce low-friction, durable, fatigue-resistant joint bearings. Cellular responses to environmental effectors, such as mechanical stress or hormones, can beneficially change the composition and assembly of these materials. This is enabled through the coupling of specific protein synthesis and degradation with the constant monitoring of mechanical function and the state of need of the organism. Long-term cellular activity within the material can enable the repair of the material upon damage by reactivation of matrix formation. These advances could create not only new membrane and biomaterial technologies but also new insights for structuring hard materials.

Rigid Structural Composites

Many of the rigid structural materials found in nature are composites comprising unusual compositions and configurations. For example, the nacreous material in mollusk shell is a segmented composite with a very low volume fraction of matrix phase in very thin layers. The ability to design and fabricate synthetic structures with similar characteristics, as well as the ability to mimic adhesion between the phases, could lead to composites with remarkable

properties, by combining outstanding strength and stiffness with improved fracture toughness compared with that of monolithic materials or current composites. In addition to practical and cost-effective fabrication techniques, an understanding of deformation mechanisms and the ability to enhance composite structural response through mechanical modeling are critical to the success of these materials.

Adhesives and Interfaces

Adhesives and interfaces play important roles in both natural and synthetic composites. Although much has been done in adhesion science and technology, there are opportunities to tailor new synthetic adhesives and unique structural architectures by way of mimicry of natural systems. Adhesives are critical in the formation, strength, and durability of composite materials as agents responsible for bonding between matrix and reinforcing phases. Advances in composites have emphasized the need for durable adhesives that would work in wet environments. Adhesives produced by organisms, especially marine organisms, suggest themselves as candidates for study, because they cure in the presence of water and resist its subversive effects.

Soft-Tissue Based Materials

Exceptional designs for "ultrasoft" materials and for interfacing soft and hard materials are found in nature with capabilities well beyond present day technology. The committee feels that exposing the physical and chemical principles that underlie the special features of these materials is certain to stimulate new approaches to design of synthetic materials, parts, and systems. Such approaches may include preparation of "self-healing" capsular materials that possess tunable and motile properties; general methods for assembly of soft organic and hard material interfaces that are mechanically, chemically, and electrically compatible; and development of membrane composites that

are based on fluid–surfactant interfaces supported by tethered polymer networks that possess permeability restriction and mechanical strength.

Control of Size and Shape (Assembly, Self-Assembly)

Inherent in the behavior of natural proteins is their assembly into structures of a given size and shape to allow the performance of a specific end-use function. This formation of parts and systems is driven by local geometry and molecular forces and does not require additional "shaping and machining" steps. The ability to design synthetic systems capable of assembling in an analogous fashion would have obvious practical impact. Some natural self-assembling systems have a defined size, such as some vesicles, while others are indefinite in extent, such as unstrained crystals. Proper function requires that system size be controlled as well as system shape. A key factor in control of system size and shape is the identification of switching mechanisms that govern, for example, the size and shape of nacreous platelets in abalone shells, as well as the thickness of the protein layers that separate the layers.

TECHNOLOGICAL OPPORTUNITIES

Biomedical Materials

There is a recognized societal and economic need for synthetic materials with appropriate mechanical and functional performance characteristic properties for use in biomedical applications. The challenges in developing a manufacturing process to produce synthetic hierarchical materials with these required mechanical properties and functional characteristics are great. First, biologic tissues have very complex compositions and ultrastructural organizations. Second, the tissue is manufactured by tissue-specific cells in situ by as yet

unknown processes, which control the production and assembly of the constituent biological macromolecules.

It is unlikely that any synthetic process can be developed in the near future that can duplicate the ability of the specific cells to manufacture and organize a hierarchical material with very fine ultrastructural features. However, a hybrid approach has been taken by some researchers, where synthetic grafts which serve as scaffolds for the specifically seeded cells, have been produced from biocompatible resorbable matrices, such as polylactic acid or copolymers of lactic and glycolic acids. Gels m e of collagen and glycosaminoglycan seeded with cells also show promise as graft materials for skin and blood vessels. Development of gels that are strong, cohesive, porous, permeable, and resorbable and that are capable of sustaining high stresses and strains and providing a supporting and protecting environment for the seeded cells is a major challenge for future biomedical researchers interested in developing synthetic hierarchical materials for clinical use.

Improved Membranes and Membrane-based Devices

Improved membrane selectivity is desirable in the areas of water purification, clothing to protect those handling hazardous materials, outdoor clothing and shelters, gas separations, industrial purification processes, etc. Coupled with this is a need for improved stability and increased lifetime for these membranes, as well as for mechanisms to reduce fouling. One approach to solving these problems is to incorporate responsive channels and self-repair ("living membranes") or self-cleaning attributes that are patterned after natural membrane systems. This requires a better understanding of membrane structures in terms of their processing and assembly. Additional areas for development include suitable substitutes for water as plasticizers in these materials, and in approaches to biomimetic . .embrane design.

Smart Materials

Natural systems have the ability to sense their surroundings and to respond to impulses or changes in conditions by changing properties or initiating repair responses. The development of smart materials, which integrate the functions of sensing, actuation, and control, can benefit greatly from lessons gleaned from the studies of these biological systems. Passively smart materials respond to external change without assistance often through phase changes or transitions in fundamental properties. Actively smart materials utilize feedback loops to recognize changes and initiate appropriate responses.

Opportunities for application of smart materials systems in structural applications generally focus on reduced component mass and adaptive functionality aimed at improving structural efficiency, durability, and safety. Examples of smart materials applications include load and vibration alleviation systems, failure sensing and repair, and shape memory. Developments in sensor development and integration of sensing and response functions with practical structures are necessary to realize the potential of smart materials.

Functionally Gradient Materials

Functionally gradient materials (FGM) are materials in which a continuous spatial change in composition or microstructure gives rise to position-dependent physical and mechanical properties that can extend over microscopic or macroscopic distances. Natural materials with functional gradients abound. Examples of materials with functional gradients that are discussed in this report include articular cartilage and bone. FGM can result in changes in composition or orientation of constituents.

Synthetic FGMs can be produced from mixtures of metals, polymers or ceramics in virtually any combination. FGMs whose properties vary in the dimension of their thickness (through thickness variations) can provide a transitional interface between dissimilar

materials or serve as coatings with optimized environmental resistance and adhesion to selected substrates. Another interesting area of research is surface gradients, where the nature of the surface is varied continuously with position. Surface gradient techniques, allowing selective deposition or coating processes, may find applications in processing or in tailored membrane or sensor applications.

The development of FGMs is still in its early stages. The biggest challenge is to scale the processes to practical size components while maintaining the precise control and consistency needed. The study of gradients in natural materials may provide direction for architectural design, fabrication processes, and potential applications for synthetic FGMs.

Design and Assembly of Complex Composite Parts

Competitive composite parts require three structural elements to be controlled in a manner that leads to a finished part that possesses the desired mechanical, thermal, and environmental properties in three dimensions. These elements are matrix uniformity, fiber orientation, and fiber-matrix surface interaction. Current fabrication methods are highly labor intensive, are not amenable to complex shape formation, and present significant problems in performance assessment. Often, machining, polishing, etc., is necessary to achieve the required finished part shape and surface characteristics. In contrast, biological systems often contain complex and sophisticated fiber-reinforced composite "parts" (examples range from trees to bones), which exhibit superb performance over extended lifetimes, are capable of healing and are produced directly as finished parts from cell-based manufacturing plants. Examination of these natural fabrication methods may provide guidance in development of "smart" composites, net shape processing, multifunctional composites, controlled orientation, and FGMs.

1

INTRODUCTION

Biological materials, such as tendon, bone, wood, and many others, are characterized by hierarchical architectural designs in which organization is controlled with striking precision on many discrete length scales, which range from the molecular to the macroscopic. These hierarchically structured materials display properties that are affected by processes operating at all levels of the length-scale spectrum. Most such materials are multifunctional and are produced in situ at room temperature and atmospheric pressure through ecologically balanced processes. Many are self-healing and thus remarkably durable even under high cyclic loading (e.g., a human knee joint), and many display properties that change, either abruptly or gradually, in response to a changing environment. Equipped to prepare only limited sets of constituent materials, organisms have evolved an astonishing array of architectural strategies to realize a broad range of structure and function.

Virtually all biological materials are bounded systems that are synthesized and processed by cells at the nanoscale. Nature makes very different systems out of similar macromolecular and inorganic constituents through the process of differentiation during development. All of these materials systems have specific hierarchical composite structures. Starting with very similar macromolecular designs, each system (e.g., tendon, intestine, cornea, bone, etc.) is assembled to serve distinct, highly specific functions.

These natural systems follow three rules for complex assemblies (Baer et al., 1992). First, the structure is organized in discrete levels

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or scales. Virtually all biocomposite systems are found to have at least one distinct structural level at each of the molecular, nanoscopic, microscopic, and macroscopic scales.

Second, the levels of structural organization are held together by specific interactions between components. Considerable evidence indicates that strong surface-to-surface interactions occur, which are caused by intermolecular covalent bonds at specific active sites or by strong van der Waals forces. Whatever the nature of the bonding between levels, adequate adhesion is required for system structural integrity.

Finally, these highly interacting levels are organized into an oriented hierarchical composite system that is designed to meet a complex spectrum of functional requirements. Furthermore, as composite systems increase in complexity, they can function at higher levels of performance. The so-called intelligent materials and adaptive composite systems result from this type of complex architectural arrangement. A hierarchical biocomposite is more than just a material out of which larger objects can be built; it is a complete structural system in itself.

Synthetic materials must be described in different terms. Free of the constraints imposed by biosynthetic pathways, materials scientists and engineers have created entirely new classes of metals, ceramics, polymers, and electronic materials with extraordinary properties. Nevertheless, many desirable features of biological materials have not yet been attained in synthetic systems. For example, synthetic materials may perform well with respect to a single figure of merit (e.g., strength) but fail to meet a more complex set of performance requirements that may include permeability, optical clarity, or frictional properties. Many synthetic materials must be processed at elevated temperatures and pressures or with the aid of environmentally burdensome organic solvents. In addition, self-healing materials and materials capable of controlled environmental response remain elusive.

This situation has prom, ted growing interest within the materials community in the lessons that might be gleaned from a careful study of biological structures and of the processes by which

they are made. At the same time, biologists have begun to bridge the materials–biology gap through the application of increasingly powerful engineering analyses of natural structures and through the direct use of organisms to make interesting new materials or their building blocks.

This report focuses on a ubiquitous feature of biological materials systems—their hierarchical architectural design. What are the advantages of biological materials that are organized on many different length scales? What mechanical properties emerge from such designs? How does the architecture relate to the fabrication of the structure by the organism? Can synthetic materials systems be made this way? If so, what advantages might be realized?

At the request of the Department of Defense and the National Aeronautics and Space Administration, the National Materials Advisory Board convened the Committee on Synthetic Hierarchical Structures to examine these issues and to review techniques related to preparing hierarchical structures that possess useful and unusual physical properties and to assess the opportunities for these structures in civilian and military applications. Although a broad range of functions are represented in biological systems, the committee concentrated on structural material systems and their properties.

The purpose of this study was to conduct case-studies by selecting natural material systems to be used as models for synthetic efforts; characterize properties, unusual characteristics, and potential end-use applications for these synthetic systems; review state-of-the-art synthetic techniques and processes for assembling synthetic hierarchical structures; and recommend research that will expedite the understanding of the complex phenomena involved, lead to increased coordination among disciplines, and provide direction for future activities in the field.

2

NATURAL HIERARCHICAL MATERIALS

Many materials systems found in nature exhibit combinations of properties not found in synthetic systems. The unique performance of natural materials arises from precise hierarchical organization over a large range of length scales. The hierarchical architectures of cellulose aggregates in wood or collagen aggregates in cartilage or tendon provide excellent examples of natural composite materials designed for multifunctional applications. Even the ultrasoft membranes surrounding cells exhibit exceptional properties that emanate from structure on many length scales. These materials display unique properties that are affected by structure and generative processes at all levels of the biological structural hierarchy. Studies of materials of biological origin invariably yield surprises that demonstrate clearly that these properties have been refined by slow evolutionary engineering.

This chapter focuses on the causal relationships between structure at each level of the hierarchy and the resulting physical properties of the material or system in question. Some principles of biomaterials design and properties are discussed and illustrated in the context of several case studies on such materials as tendon, articular cartilage, wood, and nacre. In the course of its discussions, the committee considered these and many other biological materials systems. This process led to a series of recurring observations regarding the salient characteristics of this class of materials. The

committee suggests that hierarchical materials systems in biology can be characterized by:

- recurrent use of molecular constituents (e.g., collagen), such that widely variable properties are attained from apparently similar elementary units;
- controlled orientation of structural elements;
- durable interfaces between hard and soft materials;
- sensitivity to—and critical dependence on—the presence of water;
- properties that vary in response to performance requirements;
- fatigue resistance and resiliency;
- controlled and often complex shapes; and
- capacity for self-repair.

Each of these characteristics is discussed briefly herein, with reference to selected case studies and to other hierarchical biomaterial systems.

RECURRENT USE OF MOLECULAR CONSTITUENTS

Nature uses collagen in stunningly different ways: in the crimped fibers in tendon, which absorb, store, and transmit forces between muscle and bone; in the junctions between high and low modulus materials in articular cartilage; and as components of hard materials such as bone. At the molecular level, there are relatively minor differences among the collagens in these disparate biomaterials; all are similar in amino acid composition and all occur as collagen "molecules," coils of three interwound helical polypeptides about 300 nm in length (Figure 2-1). Five collagen molecules align longitudinally with an overlap of approximately one quarter the molecular length to form a microfibril of 3.6-nm diameter. This so-called quarter stagger structure includes a gap between successive collagen molecules that gives the characteristic 64-nm banding pattern
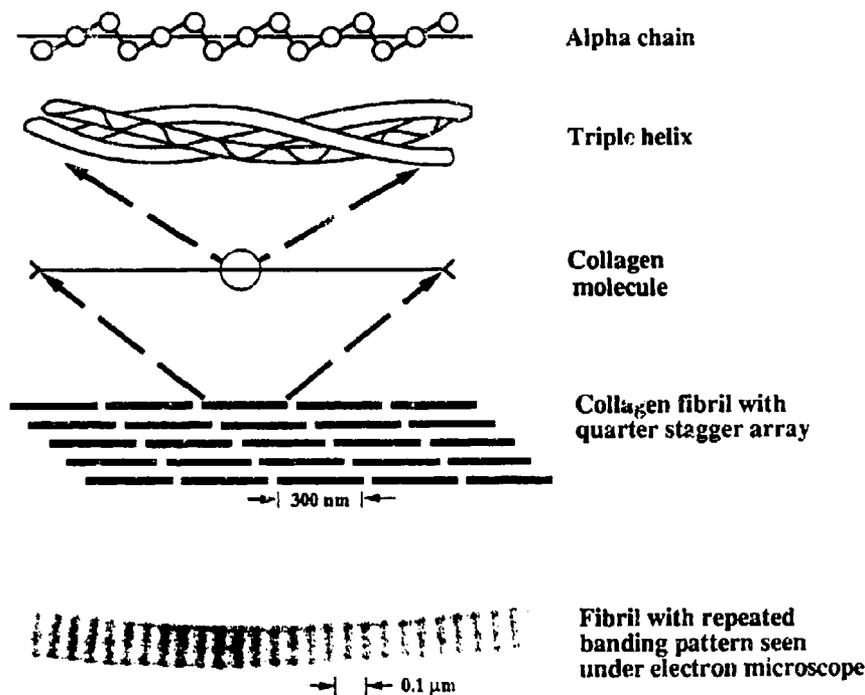
FIGURE 2-1 Building blocks of the collagen fibril. Source: Mow et al., 1992. By permission of the publishers, Butterworth-Heinemann, Ltd.

observed in the electron microscope and by x-ray diffraction (Wainwright et al., 1976). The microfibrils are then assembled into collagen fibrils that may vary in diameter from 35 to 500 nm. These basic fibrils are combined and oriented to form more highly ordered structures with a particular morphology that determines the mechanical properties of the tissue.

In the tendon, for example, the parallel alignment of crimped collagen fibers oriented longitudinally between muscle and bone provides nonlinear stress-strain behavior, with a gradual increase in stiffness upon elongation and a limiting elongation of a few percent (Kastelic and Baer, 1980). In the body of the sea anemone, on the other hand, one finds the collagenous connective tissue called the mesoglea, which is a highly hydrated, low modulus (1 kPa) viscoelastic

material that accommodates reversible extensions of more than 150 percent (see "Controlled Orientation"). And in bone (Currey, 1979, 1984), oriented collagen fibrils increase the elastic modulus, the work of fracture, and the breaking strain of the associated hydroxyapatite mineral. Although it is clear that composition (e.g., the presence of water or minerals) is critical in determining the properties of these collagenous materials, the range of behavior achieved on the basis of this single versatile family of macromolecules, because of their architecture is astonishing. The lesson for materials design is that architecture—and not composition alone—must be considered in the creation and optimization of new materials systems for use in high-performance applications. Tendon provides an instructive example.

CASE STUDY - TENDON

Tendons connect muscle to bone around a joint, thereby transmitting the force and displacement of muscle into joint motion (Kastelic and Baer, 1980). Tendons are subjected almost exclusively to uniaxial tensile loading directed along their length. Tendons must be elastic yet sufficiently stiff to transmit muscular force and capable of absorbing large amounts of energy without fracturing. For example, tendons absorb the shock to the knee joint in landing from a jump. This combination of mechanical properties is accomplished through the unique hierarchical structure of the tendon and the resulting incremental response to mechanical loads that provides initial elasticity, followed by high tensile stiffness and distributed plastic deformation to avoid catastrophic failure modes.

In the tendon, collagen fibrils are organized into ultrastructural fibrils that interact to form microscopic fibers that are packaged into larger fibers that are aligned parallel to one another and oriented longitudinally between the muscle and bone (Figure 2-2). The linkage among units at each level differs, giving an overall complex set of properties to the tendon. When these fibers are observed between crossed polarizers in the optical microscope, they have an undulating appearance. Further examination reveals the waveform to be a planar

zigzag or crimp rather than a helix (i.e., the microscopic structure does not reflect the helical conformation of the constituent collagen macromolecules). The crimp is ubiquitous in all mammalian tendons and other connective tissue types.
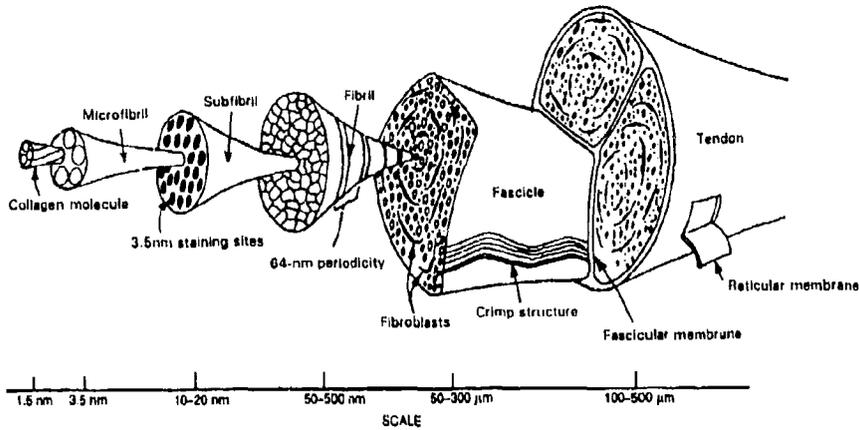
FIGURE 2-2 Hierarchical structure of the tendon. Source: Baer et al., 1992.

The response of the various elements of the hierarchical structure of the tendon is reflected in the shape of the stress-strain curve (Figure 2-3). At small tensile deformations, the curve is nonlinear, which is the case for all connective tissues. With further stretch, the curve becomes steeper and linear as a result of progressive straightening of the crimp. All normal physiological loads are confined to the nonlinear toe region of the curve. When all the fibers are straight, the modulus is high and constant. In the linear region, the fully straightened collagen fibers are further pulled elastically. If the load is released, the tendon will immediately and entirely recover its initial crimped morphology. At high strains, the tendon shows yielding and irreversible damage as the collagen fibers begin to disassociate into subfibers, fibrils, and microfibrils. Localized slippage and voiding between hierarchical levels account for the yielding observed at the macroscopic level. The hierarchical
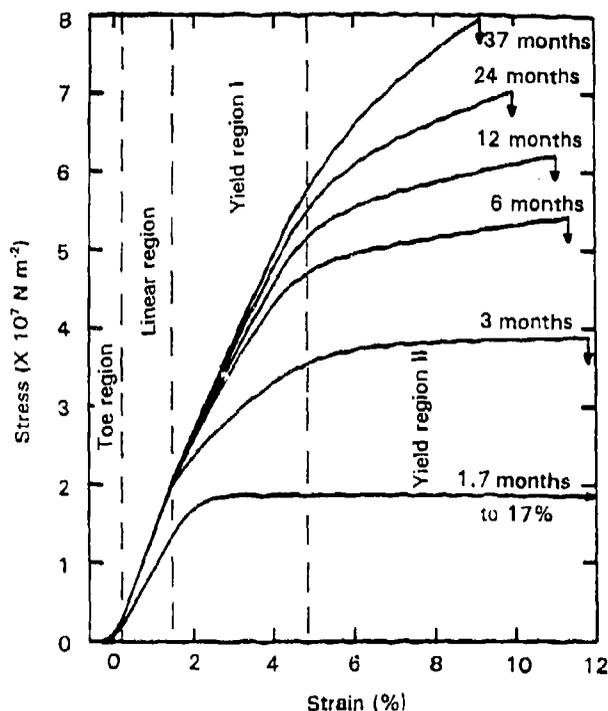
FIGURE 2-3 Stress-strain behavior of rat tail tendon as a function of age. Source: Kastelic and Baer, 1980.

design distributes stresses throughout the levels of structure, thereby minimizing dangerous stress concentrations that could precipitate failure and fracture.

The architecture of tendon provides important advantages in dynamic performance. For example, in the running human, the stresses used to launch the body off the ground at each step stretch the Achilles tendon elastically by about 4 percent. As the body leaves the ground, the leap is increased as much as 40 percent by the elastic recoil of the tendon. The total energy turnover for one foot-strike of a 70-kg man running at 4.5 m/s is about 100 J. Of this energy, about 17 J is stored as strain energy by the tendons in the arch of the foot, and 35 J is stored by the Achilles tendon. This energy storage amounts to a considerable savings in the cost of

locomotion (Ker et al., 1987). The fatigue resistance of
the tendon is remarkable as well; an athlete who runs 10
miles a day can use each Achilles tendon 6 million times
in a year without suffering permanent damage.

CONTROLLED ORIENTATION

Even a cursory examination of tissues such as bone, mesoglea,
or cartilage reveals the important role of orientation in defining the
mechanical response of structural biomaterials. In bone, for example,
the c-axes of the hydroxyapatite crystals are preferentially aligned not
only with the axes of the associated collagen fibers but also with the
directions of pull of the attached muscles. The hierarchical features
of the tissue control the fracture properties of bone, particularly the
toughness (Currey, 1984). Fracture surfaces show considerable
roughness, because the collagen fibers in neighboring lamellae of the
bone are oriented at right angles to each other. The work of driving
a crack across the interfaces made by the plates, sheets, and Haversian
systems of bone is much greater than it would be if the material were
homogeneous. All types of bone are anisotropic. For example, the
tensile strength of compact bovine Haversian bone is 148, 49, and 39
MPa in the longitudinal, tangential, and radial directions, respectively.
These differences correlate directly with the orientation of the
Haversian systems in the material.

A second example of subtle orientational control may be found
in the body of the large anemone *Metridium* (40 cm tall × 10 cm in
diameter). The body is a hollow cylindrical wall consisting of two cell
layers separated by a layer, 2 mm thick, of a collagenous connective
tissue called mesoglea (Gosline, 1971). Mesoglea is a fibrous
composite that consists of 8 percent microscopic collagen fibers
(diameter of 1–5 μm) embedded in 1 percent of a "rubbery" matrix of
an amorphous polymer with high molecular weight in 91 percent
seawater. The matrix surrounding the collagen fibers is probably a
protein-polysaccharide complex that forms a dilute gel linked into a
permanent network. The matrix accounts for both the extensibility
and the elasticity of the mesoglea; the collagen acts as a reinforcing
filler that provides rigidity to the soft matrix on short time scales. In
the outer layer of mesoglea, collagen fibers lie in a crossed helical
array and account for the ability of the animal to bend with tidal
flows without kinking. But in the inner layer, the microscopic

collagen fibers are circumferentially oriented, reinforcing the body wall to the tenfold increases in body diameter (and one hundredfold increases in body volume) that the animal undergoes in its normal behavior.

A third striking example of the role of orientation in controlling the mechanical performance of hierarchical biomaterials is provided by wood, in the second case study.

CASE STUDY - WOOD

Wood is a hydrated composite with a high specific strength and stiffr_ss, especially in the direction of preferred reinforcement orientation (parallel to the trunk) (Vincent, 1990; Wainwright et al., 1982). The fracture toughness of wood is outstanding, largely due to the hierarchical structural arrangement and the resulting failure-containment mechanisms.

Wood is composed of the high-modulus, high-strength, crystalline polysaccharide, cellulose, in an amorphous matrix of hemicellulose, lignin, and other compounds. The architecture is that of an aggregate of microscopic cylindrical cell walls of the composite, with the cylinders lying parallel to the long axis of the stem, root, or leaf. The cellulose in the cell walls has a preferred orientation that varies according to its position along the radius of the cell and hence its age in the wall. The wood of many tree species occurs in concentric growth layers of cells that have large lumens (early wood) alternating with layers of cell walls that have small lumens (late wood). Figure 2-4 shows the hierarchical scale and complexity of wood.

Wood is anisotropic and viscoelastic. Most studies on the physical properties of wood are done on oven dried timber (12 percent water saturation), but wood evolved to function in trees in its saturated (wet) state. The low density (600 kg$\cdot$m^{-3}) of timber makes it an appropriate material for many manmade contrivances. Wood and mild steel show comparable stiffness per unit weight, but the specific strength of wood is four times that of mild steel.
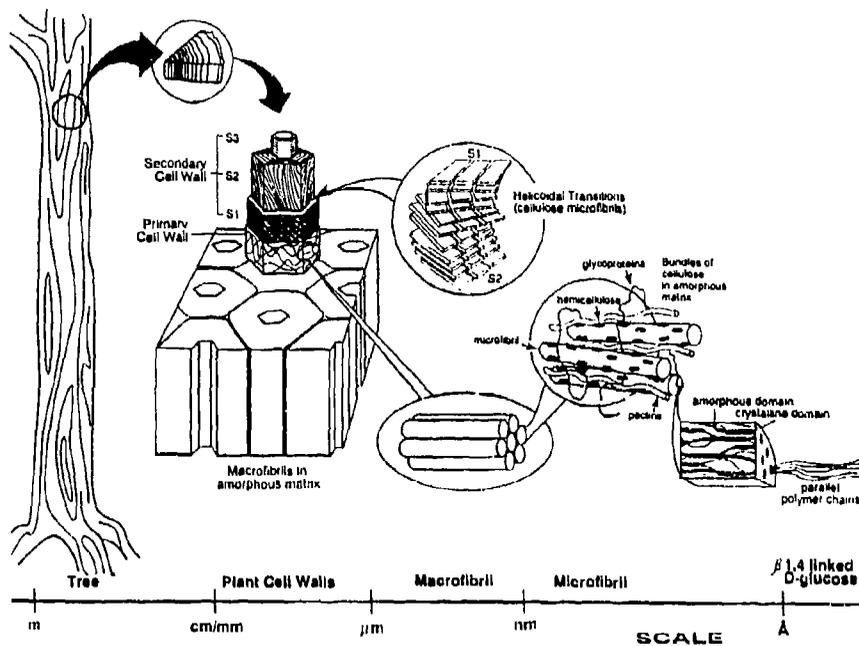
FIGURE 2-4 Structural hierarchy of cellulose in wood. (Courtesy of D. Kaplan, U.S. Army Natick Research, Development, and Engineering Center)

The most remarkable property of wood is fracture toughness that is 10 times greater than would be predicted considering volume fractions of fibers and matrix in fibrous composites. These pr̥ ̩ ̩ assume that the creation of new surface area by fi ̩r pull-out is the major mechanism responsible for fracture toughness. The mechanism accounting for the high fracture toughness for wood is helical column buckling of the cellulose fiber-wound cell wall (Jeronimidis, 1976). Interfibrillar cracks due to shearing will open and propagate longitudinally while the cylindrical wall collapses inward, which allows each cell wall to be pulled apart without being broken in two.

DURABLE INTERFACES BETWEEN HARD
AND SOFT MATERIALS

The performance of hierarchical materials systems depends critically on the formation of appropriate interfaces between structural elements of disparate scale and composition. Particularly intriguing—and challenging from the point of view of system design—are interfaces between materials of widely different stiffness (i.e., between hard and soft materials).

Nature uses a variety of strategies to make such interfaces. In bone, for example, it has been proposed that the interface between collagen and the hundredfold stiffer hydroxyapatite is formed via epitaxial crystallization of the mineral on a phosphorylated collagen template (Glimcher, 1984). In articular cartilage, collagen orientation changes from parallel to the surface in the outer zone, to a perpendicular orientation at the interface, with fibers extending into the bone (see Case Study-Articular Cartilage). And in mollusk shell nacre, the next case study, a protein-chitin "sandwich" serves to interconnect much stiffer inorganic crystals, absorbing much of the work of fracture via ductile deformation and the formation of new surface.

CASE STUDY - MOLLUSK SHELL NACRE
(MOTHER OF PEARL)

The inner nacreous layer of mollusk shells is a layered composite that has outstanding strength and hardness while maintaining remarkable fracture toughness (Jackson et al., 1988; Sarikaya et al., 1990). The high volume fraction of the reinforcing (hard) phase, compared with processible synthetic composites, allows strength and hardness to approach that of the monolithic material. The reinforcing phase is bound with a very thin layer of soft but tenacious matrix that imparts fracture toughness to the composite.

The structure of nacre is shown in Figure 2-5. Aragonite "bricks" make up layers 150–500 nm thick that are interspersed with layers of organic polymeric material 20–250 nm thick. The aragonite bricks are plate-like

single crystals with specific orientation relationships among crystals of the same layer, as well as among crystals of successive layers. The organic matrix phase is continuous throughout the material and is composed of the aminopolysaccharide, chitin, coated with a protein that promotes adhesion to the aragonite plates.

The mechanical properties of nacre are better than those of most monolithic ceramics, with fracture strength of 185 ± 20 MPa and fracture toughness, $K_{IC} = 8 \pm 3$ MPa$\cdot$m$^{1/2}$ (Sarikaya et al., 1990). The work of fracture across layers is 1 kJ$\cdot$m^{-2}, and between layers is 0.1 kJ$\cdot$m^{-2}.

Toughening mechanisms revealed by fractographic analysis of fracture surfaces and indentation cracks include (1) crack blunting and branching; (2) microcrack formation; (3) sliding and pull-out of aragonite plates; (4) polymeric ligament formation, akin to crazing, which bridges cracks; and (5) possible strain hardening and shearing of the organic material.

THE ROLE OF WATER

Water is ubiquitous in biological materials, in amounts varying from a few percent in fibrous proteins to more than 90 percent in mesoglea. Water forms strong hydrogen bonds with biological macromolecules and facilitates motion on all length scales, from molecular to macroscopic. The elasticity and toughness of many biological materials depend critically on hydration. In nacre, for example, toughness and ductility double upon hydration without significant loss of stiffness (Vincent, 1990).

Swelling pressures resulting from the presence of water in biological structures help to oppose compressive loads. In articular cartilage, for example, water constitutes 65–80 percent of the tissue and is confined in a swollen network of collagen fibers and proteoglycan aggregates. As described in the fourth case study, the resulting hydrostatic pressure accounts for most of the apparent compressive modulus of the material and provides a source of lubricating fluid, which maintains the low coefficient of friction in the joint.

FIGURE 2-5 The structure of nacre. Source: Sarikaya et al., 1990.

CASE STUDY - ARTICULAR CARTILAGE

Articular cartilage (Mow et al., 1990; 1992) is a natural hierarchical material exhibiting high strength and stiffness; functionally gradient microstructure; and outstanding friction, lubrication, and wear characteristics. Compositional and organizational characteristics provide the appropriate deformational behavior required for cartilage to function as the low-friction, wear-resistant bearing materials at the ends of long bones (hip, knee, shoulder, etc.) and sides of sesamoid or carpus bones (patella, wrist bones, etc.) in highly loaded conditions.

Articular cartilage is a porous-permeable, fiber-reinforced composite filled with fluid. The fibrous component is primarily type II collagen, and the gel matrix is made of aggregating proteoglycans. Collagen and proteoglycan form interpenetrating networks that create a strong solid matrix. Water, is by far the largest component (70 to 90 percent) of the tissue by wet weight as it is with most biologic tissues. Water contains a physiologic concentration of electrolytes that is required for osmotic equilibrium.

The collagen network is cohesive, strong, and permanent, and it provides the required tensile stiffness and strength for cartilage. These properties derive from the intrinsic properties of the collagen molecule and the hydroxypyridinium cross-links that exist between collagen fibers. The proteoglycan aggregates form a labile network that provides the compressive stiffness that results from their bulk compressive stiffness and from the swelling pressure. The swelling pressure has two components—Donnan osmotic pressure and charge-to-charge repulsion amongst fixed negative charges (COO^- and SO_3^-) on the glycosaminoglycan groups of proteoglycans.

Figure 2-6 illustrates the collagen microstructural organization of articular cartilage. Collagen content and collagen fiber orientation vary with depth from the articular surface. In the tissue, collagen content decreases and proteoglycan content increases from the surface zone to the inner zone next to the bone. Collagen fiber

orientation can be characterized in three zones: the outer surface zone has a preferred orientation parallel to the surface; the middle zone has orientation at nearly 45° to the surface; the deep zone has orientation perpendicular to the bony interface, with the fibers extending into the bone for effective anchorage. This is an excellent example of a junction between materials of high and low modulus.

Normal articular surface is textured with ripples and dimples, with characteristic dimensions ranging from 0.1 to 10.0 μm. These features function to trap pockets of synovial fluid that enhances fluid-film lubrication between the two bearing surfaces of the joint. In addition, the formation of the fluid lubricant film in joints is augmented by a circulation of water from cartilage. The high water content in the surface zone is particularly important for this self-lubrication process to develop.
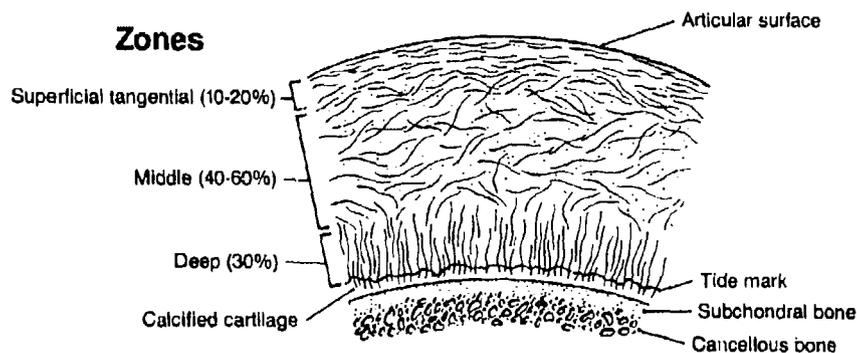
FIGURE 2-6   Ultrastructural organization of collagen fibers throughout the depth of articular cartilage. Source: Mow et al., 1992. By permission of the publishers, Butterworth-Heinemann, Ltd.

The hierarchical architecture of diarthrodial joints and articular cartilage is illustrated in Figure 2-7. The charged nature of proteoglycans and electrolytes at the nanometer scale is responsible for tissue swelling, hydration, and pre-stress in the collagen network. The molecular and ultrastructural organizations of the

collagen-proteoglycan solid matrix are responsible for the
fiber-reinforced composite nature of the tissue. The pre-
stress (or residual stress) in the collagen network that
results from proteoglycan swelling is believed to have an
important physiologic function simi'ar to pre-stressed
reinforcement bars in concrete beams. The degree of
hydration in the cartilage depends on the balance of
swelling pressure and the elastic pre-stress developed in
the solid matrix and is the most important factor
governing cartilage mechanical properties and function.

The cells in each zone of the tissue are structural
features at the microlevel, and they are responsible for
the phenotypic expression of the protein and
carbohydrate products that are required to make collagen
and proteoglycan and to maintain the specific structural
organization in each zone of cartilage throughout life.
This self-repair process is essential for maintaining the
structural integrity of the tissue. When the biologic
maintenance and repair processes fail, the cohesive
collagen-proteoglycan solid matrix weakens, cartilage
gains excessive hydration, and it fails to function as a
bearing material in the joint. In this case, diseases such as
arthritis develop. Normal cartilage has a coefficient of
friction ranging from 0.005 to 0.02. Diseased cartilage
has higher coefficients of friction. To put these figures
in perspective, the value of ice on ice is 0.01–0.1, and for
graphite on steel, about 0.1.

The complex architecture of articular cartilage
results in a joint that can endure millions of cycles, under
heavy loads (up to 18 MPa), without failure. The tensile
modulus varies from zone to zone, from 41 MPa near the
surface to 1.0 MPa near the bone. The equilibrium
compressive modulus (1.5 MPa) does not appear to vary
with zone and is provided equally by the bulk
compressive stiffness and the swelling pressure. Under
dynamic loading, very high compressive moduli have
been reported (50 MPa). This apparent stiffness is
provided largely by the pressure developed in the
incompressible water component of the tissue. Thus,
water has a major role in the ability of normal cartilage to
oppose compressive loads in physiologic conditions.
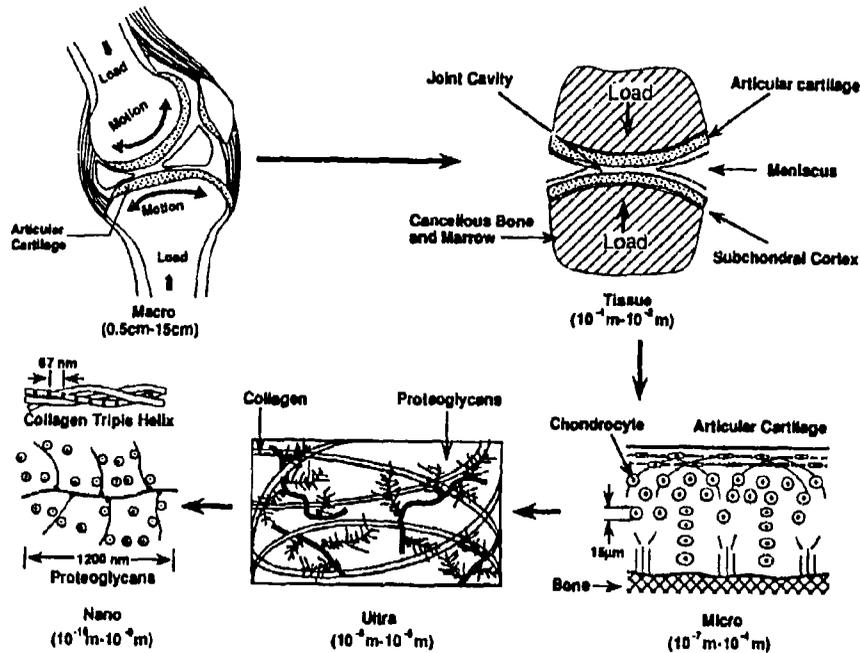
FIGURE 2-7 Hierarchical architecture of diarthrodial joints and the constituent articular cartilage. Source: Mow et al., 1992. By permission of the publishers, Butterworth-Heinemann, Ltd.

Finally, the collagen-proteoglycan solid matrix is viscoelastic, with a shear modulus that increases monotonically with frequency from 0.2 MPa at 0.01 Hz to 2.5 MPa at 20 Hz. Thus the shear stiffness of cartilage is provided by collagen within the collagen-protoglycan solid matrix.

PROPERTY VARIATION IN RESPONSE TO CHANGING PERFORMANCE REQUIREMENTS

Perhaps the most fascinating characteristic of many natural materials is their capacity to respond—via changing properties—to changes in performance requirements. For example, while the spines of the sea urchin are moving, the attached ligaments are soft and extensible, but when the animal is stimulated,the ligaments become

viscous, causing the joints to stiffen (Motokawa, 1984; Trotter and Koob, 1989). The effect is so dramatic that the calcite spines will fracture before the stiffened joints will give way to a sudden blow. The catch connective tissue of the urchin contains collagen fibers in a tendon-like parallel array. Extending into the array are axons of nerve cells whose bodies lie in a ganglion outside the tissue. These ligaments lie parallel to muscles that bend the joint at the base of the spines, allowing the animal to point its spines at aggressors or to use its spines as stiff legs for walking. Isolated ligaments deprived of calcium ions are soft, while those exposed to natural concentrations of calcium are extremely viscous. Neurotransmitters (to which the isolated ligaments are sensitive) may be produced by the attendant nerve cells to control the ionic environment and thus the mechanical properties of the ligaments.

CASE STUDY - SHARK SKIN

The skin of sharks and other fishes operates mechanically as a two-dimensional membrane that is 2-4 mm thick and formed into a pressurized cylinder (Wainwright et al., 1978). Shark skin is more than 80 percent collagen by volume. Its thick inner layer is made up of collagen fibers in 30 to 90 layers that are each 10 μm thick. Fibers in each layer are parallel, and fibers in alternating layers wrap around the animal's body in right- and left-handed helices. This makes the body a fiber-wound, pressurized cylinder. The fibers lie closely spaced in a viscous matrix of cells and other extracellular materials as yet unknown.

When the fish swims, it bends its body in left and right directions, stretching the skin 10–15 percent on the outside and compressing it 1–15 percent on the inside of the bends. Thus the skin normally functions by stretching 10 percent, even though collagen's breaking strain is about 4 percent. The crossed-helical array of fibers and the hierarchical structure of the skin permit this range of motion.

The shark's body is mostly muscle, which is a cellular viscoelastic solid of constant volume. When muscle contracts, shortening one side of the fish, it bulges

and causes an increase in pressure against the skin on that side. High modulus fibers wound helically around flexible cylinders reinforce against aneurysms that can be caused by internal pressure and allow the cylindrical body to bend without kinking.

Stress in the skin of any thin-walled cylinder equals the pressure multiplied by the ratio of the body radius to the skin thickness. Skin stress in a fast swimming shark rises with pressure by as much as 200 percent. Since the skin is only stretching by 15 percent at most, to bear the increased stress the apparent stiffness of the skin increases amazingly, by a factor of 13. Thus, during normal function, stiffness, a material property normally thought to be static, is changing according to the demands of muscle action. The increase in stiffness apparently allows the skin to act in transmission of force from muscle in the anterior parts of the fish to manipulate the tail.

It is likely that the study of biological materials capable of this kind of environmental response will reveal a rich variety of mechanisms for coupling of sensory information and the physical and mechanical properties of materials. Such studies should provide concepts useful in the design of new classes of advanced ("smart") materials with the capacity to adapt rapidly and productively to changing environments.

FATIGUE RESISTANCE AND SELF-REPAIR

Organisms are remarkably durable, especially in view of the fragility of their molecular constituents. The mechanisms by which organisms and tissues withstand damage without catastrophic failure are of interest with respect to the design of damage-tolerant materials and structures. In some tissues (e.g., in bone), durability results from a complex process of remodeling and reconstruction (Currey, 1984). In others (e.g., in cellular membranes and associated soft tissues), resistance to wear and fracture emerges from the architectural features of the structure itself.

CASE STUDY - CELL MEMBRANES AND SOFT TISSUES

The structure of cell membranes and their assembly into soft tissue can provide remarkable durability and wear resistance to biological organisms (Bloom et al., 1991; Evans, 1985; Evans and Skalak, 1980; Lipowsky, 1991). The core layer of the membranes of animal and plant cells is a bilayer in which lipids, surfactants with short alkyl polymer chains, are organized into a hydrophobic film sandwiched between hydrophilic surfaces in which other cosurfactants (e.g., cholesterol, integrin proteins, ion channels, etc.) are embedded. Adjacent to the lipid core is a scaffolding of cytoskeletal proteins (e.g., actin), which supports the bilayer through specific sites of attachment along the inner surface of the membrane. Embedded inside the cell and often within a cytoskeletal mesh, other nonstructural organelles form a visceral slurry in which many biochemical functions are carried out, such as protein and lipid fabrication and chemical energy storage and generation.

The membrane is hyperdeformable and ultrasoft with low extension modulus, for example, 0.1 to 1 kPa for the red blood cell (the modulus of soft rubber is 0.1 to 1 MPa). The lipid bilayer chemically isolates and regulates the cell interior; the cytoskeletal network provides mechanical support and controls the ability of the cell to change shape and, in some cells, to move. Large deformations are made possible by wrinkles and folds in the membrane. Cholesterol augments the cohesive and anchoring strength of the bilayer tenfold. Thus, in the red blood cell, a rigid polymer scaffolding has been interfaced with a fluid membrane to form a compatible composite that is two orders of magnitude softer than existing synthetic elastomers.

At the next higher level of the structural hierarchy, a soft tissue, such as skin or liver, can be described as an aggregate of fluid membrane capsules which is supported by internal networks that are connected to form a compatible composite that is resistant to wear and fracture. Cells are bonded together by specific molecular "welds" between integral proteins in adjacent membrane

bilayers, which provide transmission of cytoskeletal stress from one cell to the next. The lipid bilayer envelopes are thus "transparent" to stress, and the mechanical properties of the tissue arise from the network of cytoskeletons that penetrate the bilayer capsules. Intercellular connections easily translate along the fluid bilayer, and the membranous envelope readily flows to accommodate network deformation. Friction between cells is minimized by highly hydrated glycoprotein spacers.

SHAPE CONTROL

The beautiful and intricate shapes of biological structures are apparent to even the most naive observer (Figure 2-8). But perhaps even more remarkable are the mechanisms by which structural shapes are controlled in biology. The shapes of a few simple biological structures (e.g., simple viruses), are entirely determined by the interactive properties and shapes of their macromolecular components, as these govern the self-assembly of the structures. However, complex shapes emerge from small scales to large, through intricate processes of molecular and supra-molecular assembly. Molecular information in biology is translated into structural features that are orders of magnitude larger in scale, and into performance properties that serve the survival needs of the organism. An understanding of these processes offers the prospect of significant new approaches to the fabrication of complex synthetic structures.

Large biological structures consist of cells and matrices. The overall shape of such a structure is governed by the disposition of the component cells and of the matrices that some of them manufacture. The matrix-producing cells are closely apposed to existing matrix and may eventually become enveloped in matrix that they form. At any time during manufacture, the evolving shape of a biological structure is the product of multiple, successive hen-and-egg events: the cells that are currently making matrix are at specific sites because of earlier events in the development of the organism, and they, in turn, influence the sites where future cells will produce additional matrix. The number of synthetically active cells at a given site depends on earlier replication of cells by cell division; on migration of cells over preexisting structures; and on numerous genetic programs that control cell division, specialization of cells, and synthetic acitivity. In

addition, there are a variety of control feedback loops, many of which
are poorly understood. Cells can mutually influence each other
through diffusible factors, such as hormones and cytokines; cells
repond to signals from adjacent matrix; and the biosynthetic activity
of matrix-producing cells may even respond to local, repeated
mechanical stress.

From the above, it follows that the intimate relationships
between the local manufacturer of matrix components, for example,
a fibroblast cell, and the matrix to which it adheres, which may be
part of a tendon or bone, influence both the local composition and the
orientation of new matrix and, eventually the shape of the completed
tendon or bone. The local composition readily acquires a layered, or
even interwoven, structure due to repeated cycles of deposition by sets
of cells.

Shape is not only influenced by geographically different rates
of formation but also by selective removal of existing matrix or of
complex combinations of cells and matrix. Tadpoles initially make a
tail but then lose it when they turn into frogs. The whole head of a
newborn infant could fit into the skull cavity of the adult head that it
later develops into. This is partly because of selective removal of bone
from the inner surface of the skull even while more bone is added to
the outer surface during growth. The removal of existing matrix
during growth can be highly selective not only at the macroscale of
sculpting a previous shape but also at the microstructural level. For
example, the walls and ends of a tubular long bone are not
continuously solid but consist of trabeculae of bone that run along
lines of mechanical stress during average, common use. These
trabeculae are not permanently fixed but can change during abnormal
use of limbs, as with a lopsided gait after injury to the one leg. Thus
normal and pathological bone removal change the shape and structure
of an earlier biological form.

In summary, biological shape is the outcome of repeated
deposition and selective removal. A critical feature during biological
manufacture is that the microfactory, the cell, is intimately and locally
associated with the evolving matrix. Importantly, many cells function
at any one time, and the successive actions of cells are influenced by
the history of manufacture. In general, shape and size are not fixed
but change with the development and age of the organism.
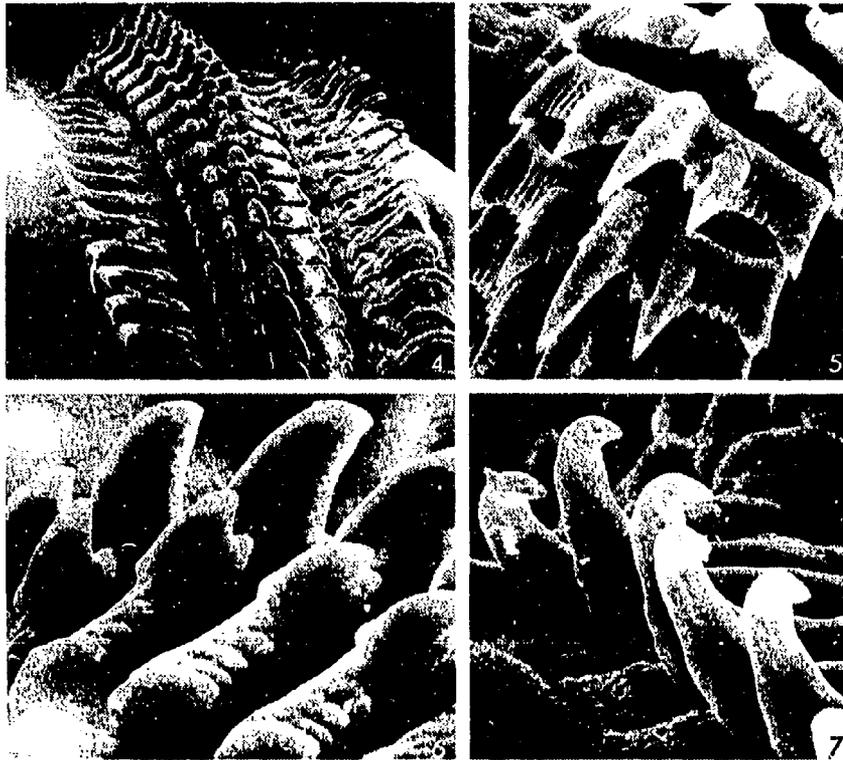
FIGURE 2-8 Scanning electron micrographs of the rasping tongue of the mollusk *Urosalpinx cinerea follyensis.* The mineralized structure contains crystalline magnetite in an ordered matrix of organic fibrils. Magnification: (a) 200x, (b) 575x, (c) 980x, (d) 980x. Source: Carriker et al., 1974.

3

SYNTHETIC HIERARCHICAL SYSTEMS

INTRODUCTION

It can be seen from the prior chapters that lessons can be learned from nature that may, if carefully deciphered, point the way to design of new classes of synthetic hierarchical materials. However, a number of caveats are in order. Vincent and Srinivasan (1992) point out "good scientists borrow ideas, but great scientists steal them. The greatness lies in realizing that an idea is worth stealing. Just as we need to know what ideas are available to be stolen from nature. . . we need to be sure that they are worth stealing. . . ." This warning is appropriate for a number of reasons. The three examples that follow illustrate some of the dangers involved in copying from nature without thorough mechanistic understanding.

First, natural materials are, more often than not, multifunctional. For example, the architecture and morphology of the cellular structures of woods provide strength in bending and compression, as well as resistance to fracture. However, channels in the structure are present that serve primarily a transport function (for nutrition, building, or repair). The nonstructural functional architectural elements of natural systems should not be routinely copied into a synthetic analog.

Next, Vogel (1992) notes that nature has a very limited range of materials with which it works. In rigid composites, these tend to be calcium carbonates, calcium phosphates, and silica. In mollusk shells, thin layers that surround the stiff ceramic constituents, such as those

in nacre, are proteinaceous. In addition, although natural composites exhibit outstanding combinations of properties, these material systems and their constituent components exhibit these properties over a temperature range too narrow for most engineering designs. It is useful to learn rules about adhesion, architecture, and composite elements in mechanical collaboration from nature and to apply them to other material components to make analogous synthetic structures. The natural constituents themselves have deficiencies in levels of properties.

Finally, the influence of moisture upon the mechanical behavior of rigid composites has been noted by Vincent (1990). Stiffness in natural rigid composite materials, such as horn and mollusk shells, diminishes with increasing moisture. However, the ductility and toughness increase dramatically as moisture content increases. With removal of the moisture, the mechanical effects appear reversible. In fiber-reinforced polymer-based composites that absorb significant amounts of moisture, stiffness decreases, and after an initial increase toughness eventually decreases. These effects are often not reversible upon removal of moisture.

In order to focus on potentially important rigid hierarchical structures, it is useful to cite the case of nacre, which, as shown in Figure 3-1, exhibits better fracture toughness than most monolithic ceramics. It also has reasonable levels of specific strength. It should be noted that nacre is a highly filled polymer-based composite, with the filler being an ordered platelet ceramic ($CaCO_3$) phase in the form of flat hexagons. Other mollusk shells with different structural morphologies, such as prismatic and crossed lamellar (like plywood), are also highly filled polymer-based composites and also have interesting properties (Vincent, 1990), but they have not been studied to the extent that nacre has. Other rigid biological materials that have been studied include wood (Jeronimidis, 1980) and nut shells (Vincent, 1993); the latter have been studied less extensively than the former. Modeling in these complex structures is still at a fairly early stage.

Detailed studies of nacre show a wide range of micromechanisms of deformation and failure that have been observed in high-
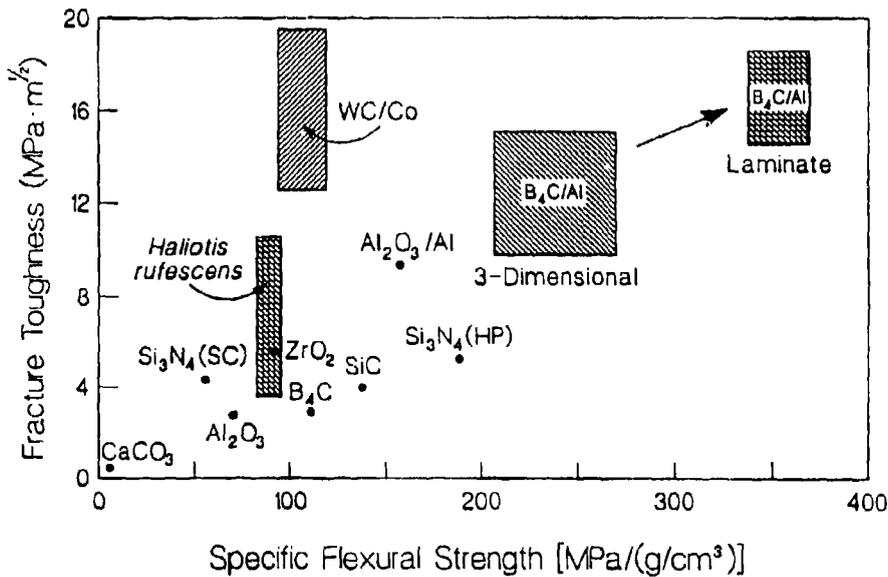
FIGURE 3-1 Fracture toughness versus specific flexural strength for abalone (Haliotis rufescens) shell nacre compared with monolithic ceramics and composites. Source: Sarikaya and Aksay, 1992.

performance structural composites. A schematic example of the structure of nacre is shown in Figure 3-2. The toughening mechanisms revealed by fractographic analysis of fracture surfaces and indentation cracks include crack blunting and branching; microcrack formation; sliding and pullout of aragonite plates; polymeric ligament formation, akin to crazing, which bridges cracks; and possible strain hardening and shearing of the organic material. The challenge is to design synthetic discontinuous laminates that use as an example the architecture of nacre; that is, (1) lamination of the component phases should form a highly ordered microstructure; (2) the thick phase should have high hardness and be surrounded by the thin phase, which should be softer, tenacious, highly plastic, and capable of strain hardening; (3) interfaces should be strong but tailored so that delamination occurs before cracking across the stiff, brittle component; and, (4) no continuous path for easy fracture

4 microns

0.5 microns

STRUCTURE OF ASSEMBLY

Aragonite

Protein

COMPOSITION (BY VOLUME)

Aragonite 95%
Protein   5%
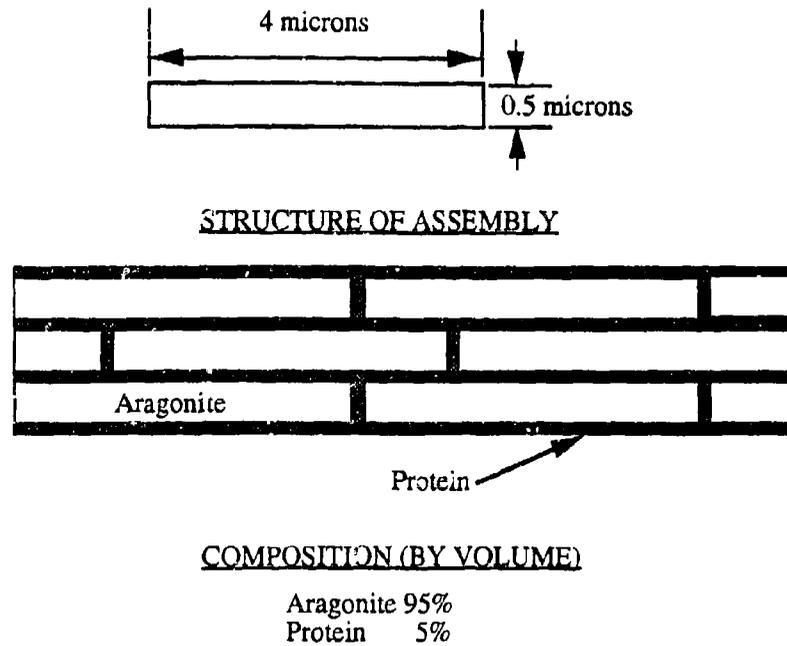
FIGURE 3-2 Structure of nacre (schematic).

should be presented (no interfaces should line up along directions of loading).

When synthetic materials are manufactured with an emphasis on tailoring their properties through microstructural control, the extent of this control is generally at a specific length scale. For instance, the mechanical properties of most metallic materials are controlled through the manipulation of dislocations at the nanometer length scale, whereas the mechanical properties of ceramic materials are controlled through the propagation of cracks that are initiated from defects of micrometer length scales. For composites that are composed of two constituents, often of quite different character, the controls are much more complex even though mechanistic understanding in many instances is reasonably well in hand.

In contrast, many biologically produced materials, as discussed in the preceding section, are very complex in structural design at a spectrum of length scales that vary from atomic to macroscopic dimensions. These hierarchically structured materials display properties that are affected by processes that operate at all levels of the length scale spectrum.

It is interesting to note that when attempts are made to engineer composites with performance-driven functions similar to those found in biological materials, the architectural design of the man-made materials also starts to display similar hierarchical features and multifunctionality. For instance, the architecture of fiber-reinforced automobile tires, which are designed to perform a multitude of functions, is very similar to the hierarchical design observed in intestinal tissue or elephant trunk. Several important classes of synthetic materials systems, defined by dimensionality, in which hierarchical architecture plays an important role are described in this chapter. The approach taken is to describe synthetic examples in one, two, and three dimensions.

ONE-DIMENSIONAL HIERARCHY

Polymeric Fibers

All oriented polymers (net axial orientation function $>$ ~0.7) possess a microfibrillar morphology. Synthetic fibers make up the largest group of oriented polymers, and all possess a hierarchical structure in the sense that they possess a repeat of fiber symmetry structure from the molecular to the macroscopic. The observation of hierarchical structure in synthetic fibers, as manifested in a series of district fibrillar substructures that have characteristic diameters in range from Angstroms to microns, is analogous to naturally occurring systems such as tendon, as described in Chapter 2 (Figure 2-2). A summary of microfibrillar and hierarchical dimensions noted in synthetic fibers is shown in Table 3-1.

The microstructure of synthetic fibers is made up of crystalline and noncrystalline elements. The choice of polymer and the details of the processing conditions control the ratio of crystalline to noncrystalline units, the net orientation associated with each phase (or subphase), and the connections between them. Synthetic fiber processing will be dealt with in more detail in Chapter 4. The microstructure of the typical 100-Å-diameter microfibril can be described as an array of crystalline and noncrystalline elements in series, as shown diagrammatically in Figure 3-3. The crystalline portions of the fibril are characterized by size (normally hundreds of angstrom by about 100 Å), net orientation, and nature of the crystal–non–crystal interface. While the equilibrium polymer crystal is composed of fully extended chains, kinetic conditions during practical crystallization almost inevitably cause the chains to fold, forming thin lamellar structures with the chains parallel to the thin dimension. While the regular nature of this folding and the concentration of tie molecules between lamellae are still debated in the literature, it is clear that tie molecule formation and less regular fold surfaces are aided by fast crystallization and chain orientation during or prior to the crystallization event. The thickness of lamellar crystals is a function of the temperature and time of crystallization, and lamellar crystals are st   ⌐ perfecting and thickening during annealing. The none. y⌐   ⌐tion of the fibril is characterized by an orientation parameter and   concentration of chains that serve as interfibrillar tie ⌐ ⌐cu,   ⌐ convenience and utility in property correlations, the no⌐ ⌐rystalli⌐.e portion of the fibril is often divided into two parts, an unoriented fraction (chains having end-to-end distance associated with the unoriented chain) and an oriented fraction that is characterized by an orientation parameter. The tie molecule concentration is difficult to measure explicitly and is usually deduced from thermomechanical measurements. In addition to these elements, microfibrils are linked together by intramolecular tie molecules. In highly oriented fiber structures, these chains are often fully extended and are referred to as the "extended chain" fraction in many models (see, for example, Ward, 1975). When all of these elements are put into a model of fiber microstructure, what often emerges is a

TABLE 3-1 Microfibrillar and Hierarchical Dimensions in Angstrom Units in Synthetic Fibers (Tucker and George, 1972)

	Basic Fibril	Microfibril		Fibril	Macrofibril
Cellulose and derivatives	30-75	100-350, 350-500		800-4,000	-
Protein fibers	30-100	100-250, 280-500		800-1,200	36,000
Polyacrylonitrile	50	150	450	3,000-4,000	30,000-40,000
Polyamides	30	100-200, 400-500		2,000-5,000	30,000-40,000
Polyester	-	100-200	400	1,200-5,000	30,000-40,000
Polyethylene	-	100-200, 400-500		2,000-3,000	-
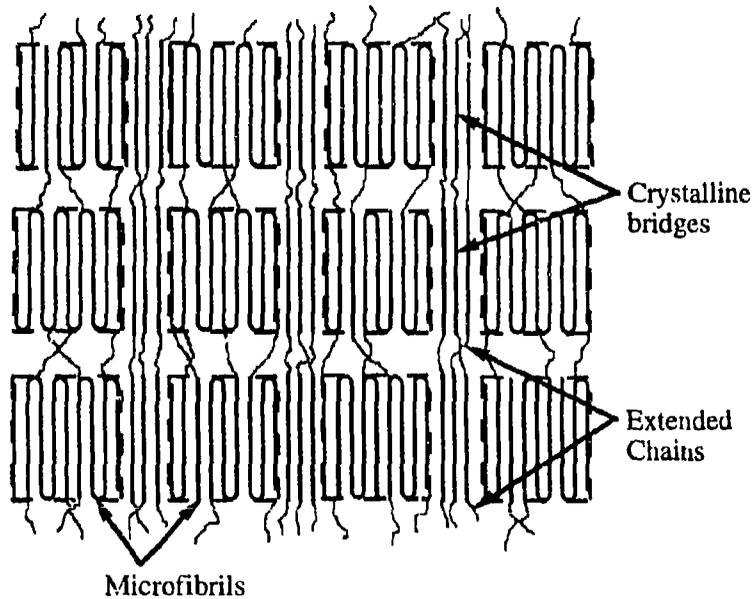
FIGURE 3-3 Microfibrillar structure with noncrystalline extended chain.

hierarchical structural array of interconnected fibrils in parallel, with each fibril composed of crystalline and noncrystalline elements in series.

Carbon Fibers

Carbon fibers are produced through the orientation and subsequent thermal decomposition of hydrocarbon precursors (Edie and Stoner, 1993). The dominant precursors for commercial carbon fibers are polyacrylonitrile (PAN) and pitch.

Carbon fibers are composed of 99.9 percent pure carbon arranged into graphitic crystallites. As shown in Figure 3-4, the graphitic layer planes form imperfect crystals, referred to as turbostratic graphite, with slightly offset layer planes and increased interlayer spacing compared with pure graphite crystals. The fundamental properties of carbon fibers are a direct result of the carbon crystal structure and orientation. The layer plane orientation parallel to the fiber axis provides the high axial stiffness and strength because of the strong chemical bonds in the graphite layer planes. However, weak van der Waals bonds between layer planes lead to significantly inferior strength and stiffness normal to the fiber axis.

PAN-based carbon fibers exhibit a fibrillar microstructure similar to that of the solution-precipitated PAN fiber precursor. The structure of a PAN-based carbon fiber has been modeled as an undulating ribbon structure of folded and interlinked layers, with the amplitude of undulation increasing from the fiber surface to the interior (Diefendorf and Tokarsky, 1975; Johnson, 1987). A schematic representation of the undulating ribbon model is shown in Figure 3-5. As a result of the structure of the precursor, PAN-based carbon fibers have a relatively low degree of axial orientation and low graphitization compared with pitch fibers.

The microstructure of pitch-based carbon fibers is dictated by fiber spinning conditions and the resulting structure of the pitch mesophase precursor. Pitch fibers generally exhibit an extended graphitic-layer structure with high axial orientation and high
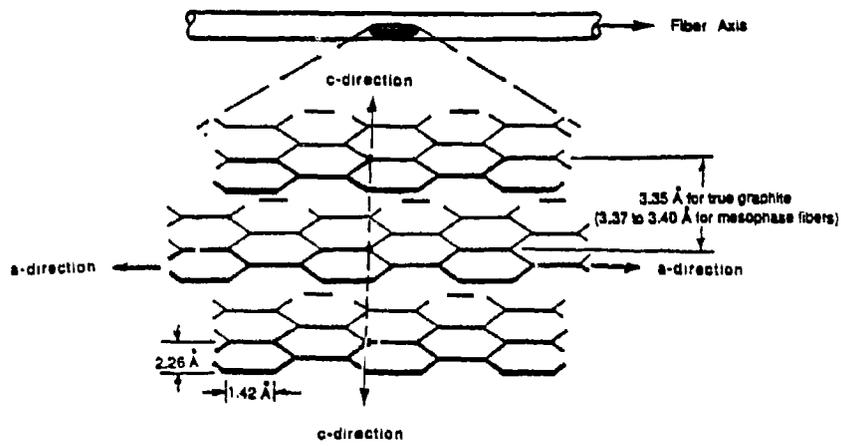
FIGURE 3-4 Structure of graphite and its approximate orientation in carbon fibers. Source: Edie and Stoner, 1993.
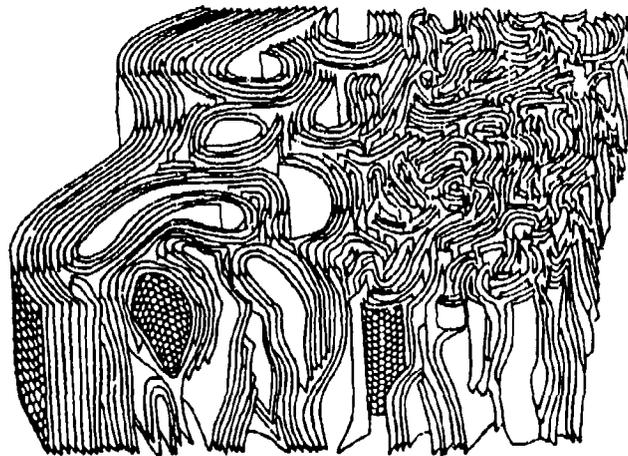
FIGURE 3-5 Schematic representation of undulating ribbon model of PAN-based carbon fiber. Source: Johnson, 1987.

graphitization compared with PAN-based fibers. An example of the variation in pitch fiber microstructure can be seen when the flat-layer structure exhibited by Amoco's Thornel pitch fiber is compared with the folded-layer configuration observed in Kashima's Carbonic pitch fiber (Endo, 1988). This is shown in Figure 3-6.

Neither PAN- nor pitch-based fibers have optimized mechanical properties (Edie and Stoner, 1993). PAN-based fibers, with their small crystallite size and imperfect orientation (caused by folded microstructure), have high strength and strain to failure but have relatively low stiffness compared with pitch fibers. In contrast, pitch-based fibers, with their high orientation and extended layer structure (large crystallites), have high modulus but lower strength and strain to failure than PAN fibers. Properties are compared in Table 3-2. Fibers from both PAN and pitch have poor compressive strength due to the low transverse strength, the deleterious effect of defects, and buckling instability. There are indications that irregularly shaped fibers could enhance compressive strength by increasing buckling stability and improve adhesion in composite applications (Edie and Stoner, 1993).

Flat Layer   Folded Layer

(a) Thornel   (b) Carbonic
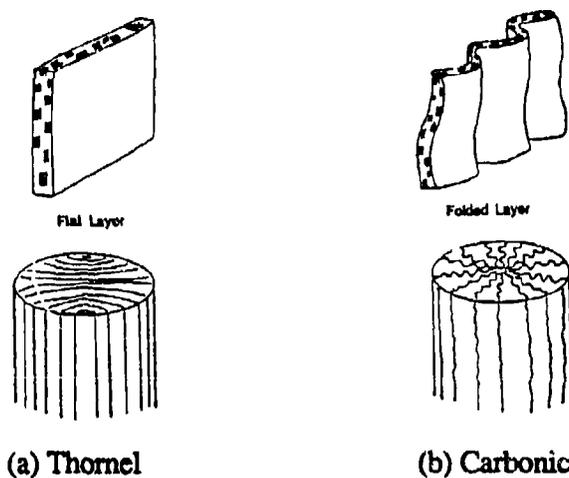
FIGURE 3-6 Microstructure for two types of pitch-based carbon fiber. Source Endo, 1988.

TABLE 3-2 Properties of Pitch-Based and PAN--Based Carbon Fibers

Fiber Name		Tensile Strength (GPa)	Tensile Modulus (GPa)	Failure Strain (%)	Inter-layer spacing d_{002} (nm)	Crystallite size L_a (nm)
PITCH-BASED FIBER						
Thornel[a]	P100	2.2	690	0.3	0.3392	24
	P120	2.4	830	0.3	0.3378	28
Carbonic[b]	HM50	2.8	490	0.6	0.3423	13
	HM60	3.0	590	0.5	0.3416	15
	HM80	3.5	790	0.4	0.3399	18
PAN-BASED FIBER						
Torayca[c]	M46	2.4	450	0.5	0.3434	6.2

[a]Amoco Performance Products, Inc. [b]Kashima Oil Co. [c]Toray Co.
Source: Endo, 1988.

TWO-DIMENSIONAL HIERARCHY

Many examples exist of advances in the properties and performance of laminate materials (Wadsworth and Sherby, 1980). Early classical work on steel laminates was the basis for Damascus steels, which were developed in the Middle East during the late iron age, more than 2000 years ago. The metallurgy that produced Damascus steel is based on a simple thermomechanical cycle that forms a composite microstructure of tough martensite containing ultrafine participates with hard strings of carbides decorating prior austenite grain boundaries. Many variations of these iron-based microstructures have since been developed by modifying thermomechanical treatments, most notably by "composite lamination," which incorporates both pure iron (soft and tough) and high and medium carbon steels (hard and strong). For example, the body of the samurai sword blade illustrated in Figure 3-7 is a hierarchical structure consisting of a soft inner core (ferrite) with a hard outer core (low-carbon martensite). The structure is formed through repeated folding and hammering of a laminated blank.

The most notable recent successes in metallic composite systems have been with the laminate materials studied by Sherby and his colleagues (Kum et al., 1983; Sherby et al., 1985, 1990). For example, it was shown that many-layered composites of ultrahigh carbon steel (UHCS) with mild steel, processed by low-temperature roll-bonding procedures, exhibit remarkable notch-impact properties (Kum et al., 1983). This result is attributable to notch blunting by delamination at the interfaces of the dissimilar layers during impact testing. Such delamination and toughening is also seen in the fracture of nacre (Jackson et al., 1988).

FIGURE 3-7 Cross-section of a Japanese sword blade (18th century). The white area near the edge is martensite. This merges gradually into dark-etching pearlite and a soft iron core. Source: Smith, 1965; courtesy of Museum of Fine Arts, Boston.

In other classes of materials, Aksay and his colleagues have achieved success in the development of hybrid laminated materials, which are based upon both ceramics and metals (cermets) and ceramic/polymeric materials (Yasrebi et al., 1990; Sarikaya et al., 1990). Tape casting and liquid infiltration were employed for processing, and in both examples, the laminated composites showed increases of up to 50 percent in both fracture toughness and fracture strength.

In the case of polymeric laminates, Baer and co-workers have been able to improve toughness and ductility as the layer thicknesses were decreased in polycarbonate and styrene-acrylonitrile copolymer (SAN) sandwiched sheets (Ma et al., 1990a,b). As the layer thicknesses decreased (with total thickness and composition held constant), fracture strain increased. When the layers were thicker, individual layers exhibited behavior characteristic of the bulk. SAN crazed or cracked, while shear bands initiated in polycarbonate from the craze tips (Figure 3-8). As the layer thickness decreased, crazing or cracking of the SAN was suppressed, and shear bands that extended through several layers produced shear yielding of both polycarbonate and SAN (Figure 3-9).
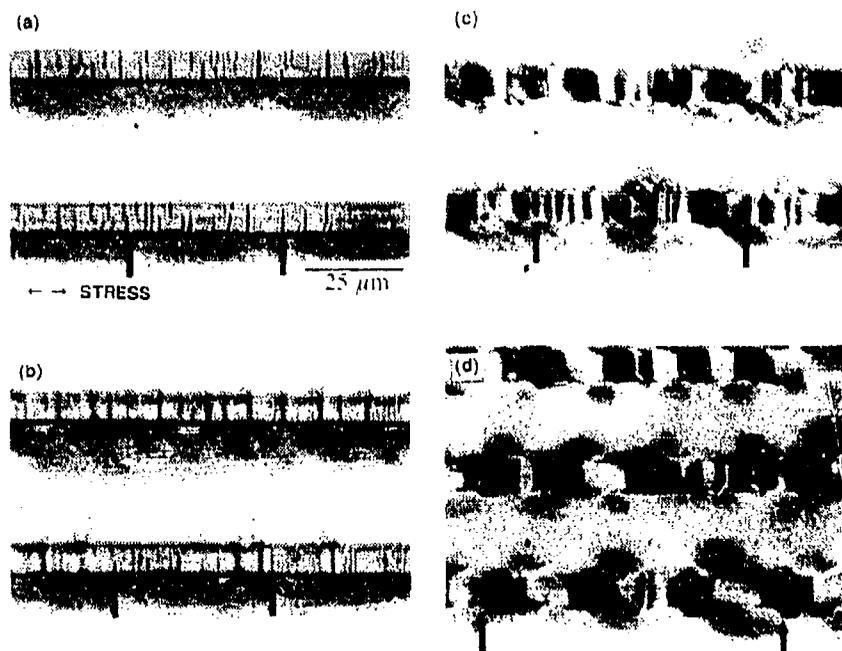
FIGURE 3-8 Optical micrographs showing microdeformation of the 49-layer composites. Micrograph progress from (a) to (d), showing increasing strain. The arrows on each micrograph mark the same region of the specimen. Source: Ma et al., 1990a.
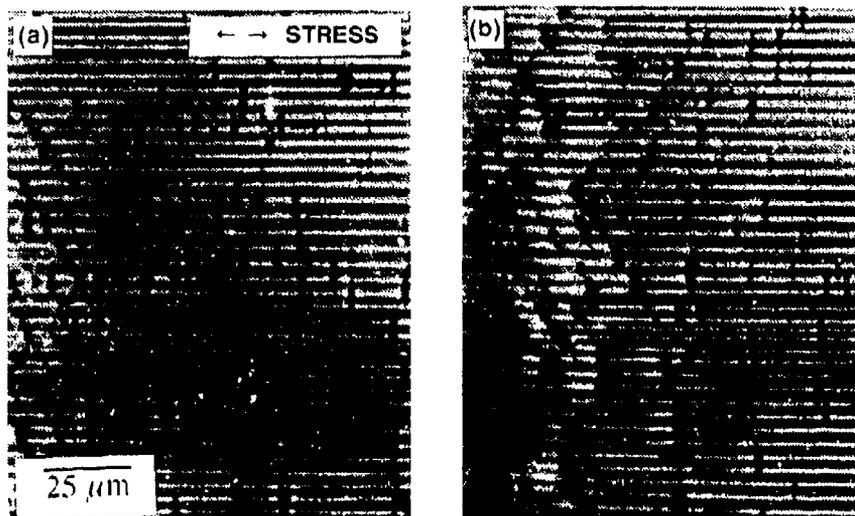
FIGURE 3-9 Detail of the necking region of the 388-layer composite; (a) and (b) show progression of the neck from left to right. Source: Ma et al., 1990a.

Calculations showed that, when the layer thickness is sufficiently small, impingement of a polycarbonate shear band on the interface creates a local shear-stress concentration. As a result, the shear band continues to grow through the SAN layer, and subsequently, at the point of instability, shear yielding can occur in both polycarbonate and SAN layers. This is shown schematically in Figure 3-10.

Improved toughness has been observed in layered biological materials, such as insect cuticle (Vincent, 1990), and crazing, microcracking, and other failure modes during deformation have been observed in other natural materials, such as woods and mollusk shells (Mayer, 1992).

THREE-DIMENSIONAL HIERARCHY

The most complex synthetic hierarchical systems are those with three-dimensional hierarchies. In this section examples are given of diverse areas of effort including metallic, ceramic, polymeric, and hybrid composites.
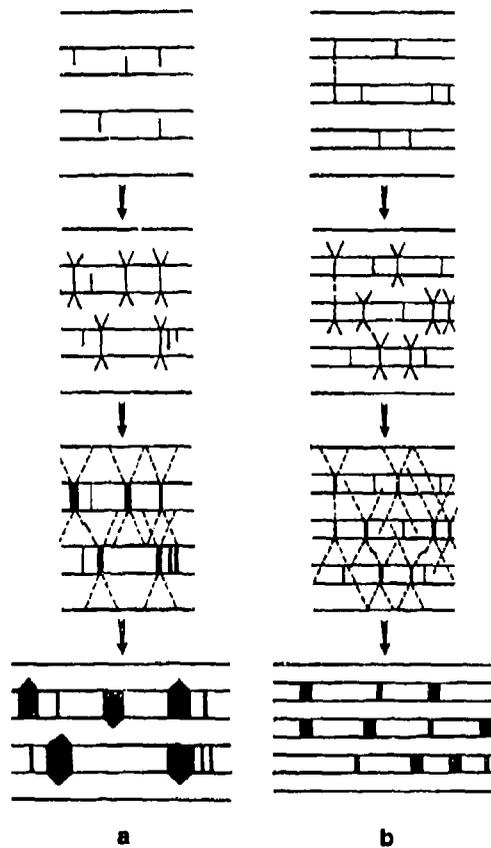
FIGURE 3-10 Schematic representation showing microdeformation in the microlayer composites with increasing strain: (a) 49- and 194-layer composites and (b) 388- and 776-layer composites. Source: Ma et al., 1990a.

Metallic Composites

Many examples exist of the strengthening of metallic materials by addition of second phases. A review of the effects of such phases was done forty years ago (Dorn and Starr, 1954). Much research and development, and the achievement of many practical alloys used by industry, has resulted from efforts on precipitation hardening and

dispersion hardening.   The factors of importance that control mechanical behavior in such materials are the size, shape, number, and distribution of second-phase particles; the strength, ductility, and strain-hardening behavior of the matrix and the second-phase; the crystallographic relationship of the phases; the interfacial energy; interfacial bonding; and the effects of internal stresses that result from forming of the composite (Dieter, 1976). It is not possible to vary these factors independently. Nonetheless, precipitation-hardenable aluminum alloys and dispersion-strengthened nickel-based alloys have been of practical use for many years.   The effectiveness of strengthening methods used in such alloys was realized some years ago and is shown by example in Figure 3-11. This plot shows critical roles of reinforcement size, aspect ratio, and volume fraction in determining yield strength of a variety of metallic composites that are reinforced by ceramic and metallic particles and fibers. More-recent work shows higher levels of strengthening that can be achieved by these methods, but the trends were demonstrated early in the evolution of composite materials.

Other composites have been formed in metallic systems by directional solidification. Table 3-3 demonstrates part of the range of reinforcements available in three-dimensional metallic composites.

In recent years, advances have been made in three-dimensional metal-matrix composites that are produced by both powder and casting routes. Examples of the latter are the DURAL™ aluminum alloy composites with silicon carbide or aluminum oxide particle reinforcements.

Textile-Based Structural Composites

The driving forces for three-dimensional high-performance structural composites have been aerospace programs such as the National Aerospace Plane, the Space Station, and the Space Shuttle. High levels of mechanical strength, stiffness, and damage resistance are generally required.   The composites are polymer-matrix composites, ceramic-matrix composites, or carbon-carbon composites.

FIGURE 3-11 Effect of particles and fibers on composite strengthening, σ_{cy}/σ_{my}, at room temperature. Source: Sutton and Chorne, 1965.

TABLE 3-3 The Microstructure and Crystallography of Directionally Solidified Composites

Composite	Type of Structure	Crystallographic relationships
Ag-Cu	Lamellar	Interface $\parallel$ $(211)_{Ag}$ $\parallel$ $(211)_{Cu}$ Growth direction $\parallel$ $[110]_{Ag}$ $\parallel$ $[110]_{Cu}$
Al-CuAl$_2$	Lamellar	Interface $\parallel$ $\{111\}_{Al}$ $\parallel$ $\{211\}_{CuAl_2}$ $<110>_{Al}$ $\parallel$ $<120>_{CuAl_2}$
Al-Al$_3$Ni	Rods	Growth direction $\parallel$ $<010>_{Al_3Ni}$ $\parallel$ $<110>_{Al}$
Cd-Zn	Lamellar	$(0001)_{Cd}$ $\parallel$ $(0001)_{Zn}$ $[01\bar{1}0]_{Cd}$ $\parallel$ $[0110]_{Zn}$ Growth direction $\parallel$ $[1120]$
Co-CoAl	Lamellar/rods	Growth direction $\parallel$ $[10\bar{1}]_{CoAl}$ $\parallel$ $[112]_{Co}$ Interface $\parallel$ $(101)_{CoAl}$ $\parallel$ $(111)_{Co}$ $[010]_{CoAl}$ $\parallel$ $[110]_{Co}$
Fe-Fe$_2$B	Square rods	Not known
Ni-Ni$_3$Nb	Lamellar	Interface $\parallel$ $(\bar{1}11)_{Ni}$ $\parallel$ $(010)_{Ni_3Nb}$ Growth direction $\parallel$ $[110]_{Ni}$ $\parallel$ $[100]_{Ni_3Nb}$
NiAl-Cr	Rods/lamellar	Interface $\parallel$ $\{112\}_{NiAl}$ $\parallel$ $\{112\}_{Cr}$ Growth direction $\parallel$ $<111>_{NiAl}$ $\parallel$ $<111>_{Cr}$

Source: Hogan et al., 1971.

Three-dimensional composites often exhibit much greater energy absorption than laminates of the same materials. For example, a three-dimensional braided polyetheretherketone/carbon thermoplastic composite showed substantially greater energy absorption than a laminate of the same materials (Hua and Ko, 1989). Textile preforms are the structural backbones of many of the three-dimensional architectures noted in Figure 3-12. An example of the effect of fiber architecture on the strengths of several glass-reinforced polymer configurations is shown in Figure 3-13.

Linear

Planar (2-D)

3-D

Discontinuous (spun)   Continuous (filament)

Woven   Knit   Braided

Woven   Knit   Braided   Nonwoven

Biaxial   Triaxial

Biaxial   Triaxial

Angle Interlock   Triaxial

Core

2 Step   3-D   XYZ

Multiaxial

Multifilament   Monofilament

Weft   Warp

MWK   Fully fashioned weft knit

Flat   Twisted   Textured

6-ply impaled   4-ply unimpaled
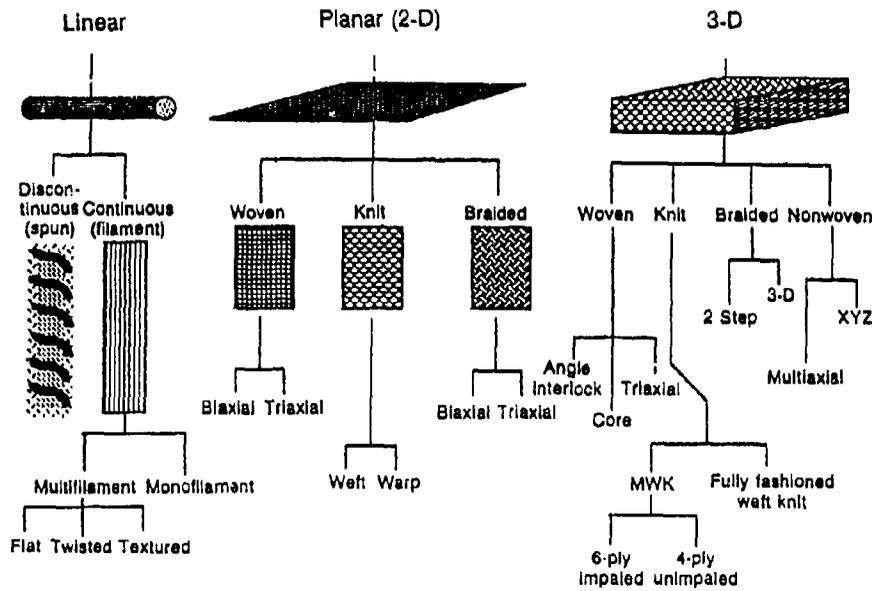
FIGURE 3-12 Classification of fiber architecture. Source: Ko, 1989. Reprinted by rmission of the American Ceramic Society.
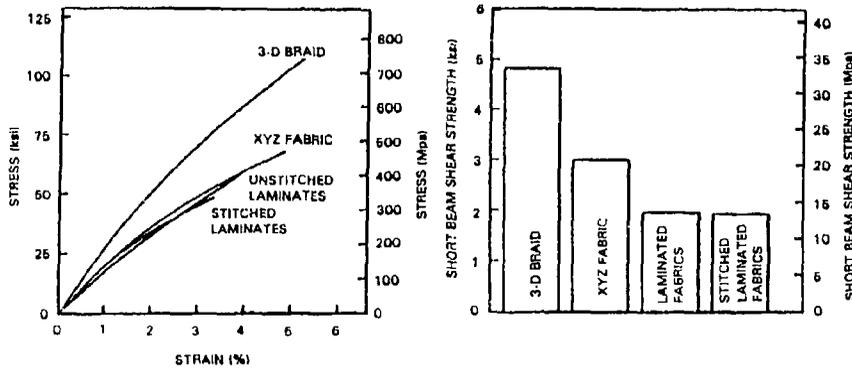
FIGURE 3-13 Effect of fiber architecture on the tensile and shear properties of e-glass/vinylester composite. Courtesy F. K. Ko, Drexel University.

Tires

Tires are highly complex engineered composite structures designed to perform diverse functions for the vehicle to which they are attached. Tires must survive for long periods of time (thousands of hours) under conditions of relatively high-frequency tension-compression cycles, with variable internal air pressure, at temperatures varying between -30 and +45°C. A typical tire construction is shown diagrammatically in Figure 3-14. Key material elements in the tire are (1) the rubber matrix, which provides friction with the road surface and prevents air diffusion; (2) the reinforcing fibers (typically highly oriented poly(ethyleneterephthalate), Nylon, Rayon, etc.), which restrict the lateral tire deformation under load; and (3) the reinforcing belts (typically high modulus fiber such as steel, glass, aramid), which restrict radial tire deformation under load.

Tires are hierarchical in the sense that they represent a multilayer composite construction, with the reinforcing layers comprising fabrics woven from twisted (usually three ply) cords, each ply of which may contain hundreds of filaments with diameter of about 20 μm (possessing a microfibrillar structure). Between the fabric layers are the soft rubbery matrix and the bonding interphase. Fabric orientations are controlled to impart the necessary mechanical performance to the tire structure.

Adhesives and Interfaces

It is important to stress the critical roles, in both synthetic and natural composites, of adhesives and interfaces. Although much has been done in adhesion science and technology, there are excellent opportunities to tailor new synthetic adhesives and unique structural architectures by way of mimicry of natural systems.

In the context of this report, there are two critical aspects of adhesives research that deserve attention. First, adhesives play a critical role in the formation, strength, and durability of composite materials as agents responsible for bonding between matrix and fiber.
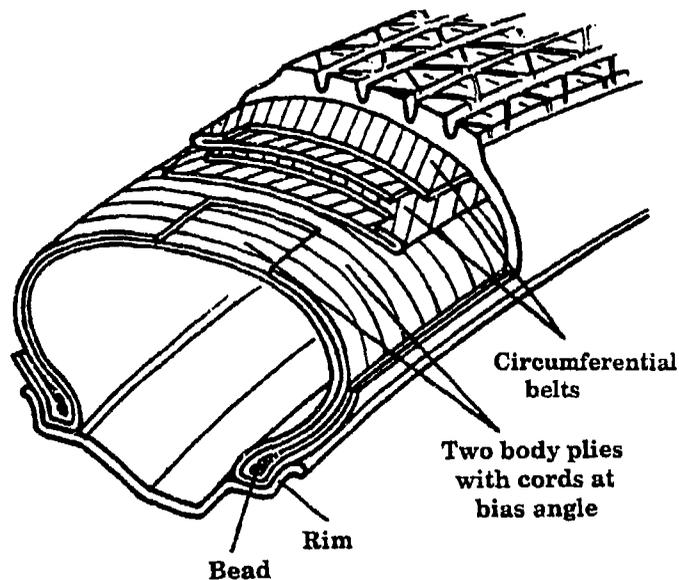
FIGURE 3-14 Typical tire construction.

The critical need for research to produce durable adhesives that would work in wet environments has been cited (NRC, 1984), and recent advances in composites have further emphasized this need. Adhesives produced by organisms, especially marine organisms, suggest themselves as candidates for study, because they occur in the presence of water, and nature has designed them to resist its subversive effects.

ADJUSTABLE VARIABLES AND THEIR INFLUENCE ON MECHANICAL BEHAVIOR OF SYNTHETIC MATERIALS

Due to the complexity of composite and heterophase materials, issues of scale, interaction, and architecture must be considered to obtain an adequate descrip.)n of the solid-state structure to describe or predict end-use properties. This level of complexity requires "systems methodologies that are amenable to modeling, analyzing and optimizing" (Haimes, 1977) these complex materials. By considering

the overall hierarchical material as a system in its use environment, it should be possible to optimize the structure-property-processing characteristics.

The advent of new processing methods that have been developed over the past four decades for synthetic metallic, ceramic, polymeric, and composite materials offers the prospect of a wide range of control of mechanical properties such as strength and fracture toughness. The key importance of grain size in determining strength was illustrated many years ago for metallic materials in the Hall-Petch relationship, which showed that the yield strength was related to the grain size:

$$\sigma_y \propto d^{-\frac{1}{2}}, \qquad (Eq.\ 3\text{-}1)$$

where d is grain size

and σ_y is yield strength

The ability of materials scientists to create finer and finer levels of scale in the architecture of materials has increased during the past few decades. Novel materials synthesis and processing, as discussed in the next chapter, has played a key role in the development of modern synthetic materials. Variables critical to material properties include:

- atomic lattice design;
- nanostructures and boundaries;
- cells and other substructure (size, morphology, structure, orientation);
- grain size, orientation, morphology, and structure;
- particle and precipitate coherence, shape, and distribution;
- orientation distributions;
- phase relations and morphologies;

- design of interfaces; and
- phase transformations.

By and large, it has not been possible to independently control these critical variables.

Design and Analysis of Synthetic Composite Systems

Understanding and analyses of the mechanical response of synthetic composite materials has advanced greatly during the past four decades. It is not the purpose of this report to provide an exhaustive review here, and the reader is referred to cited references for more in-depth treatment of composite mechanics. In some cases, the design of synthetic composites may be tailored in ways that nature cannot accomplish. Furthermore, the analyses of fairly complex structural arrangements have generally shown good agreement with experimental mechanical property data. On the other hand, sufficient, or even crude understanding of the behavior of segmented composites, such as the nacreous structure of Figure 3-2, or the more complex discontinuous combinations, such as nacreous and prismatic architecture that are often found together in sea-shells, has not been acheived. Multifunctional composites make up another emerging area in which little work has been done.

Some simple approaches to analysis of synthetic composites, along with the beginnings of application of these analyses to natural composites, are described in the following sections.

Mechanical Behavior of Rigid Composite Materials

The main purposes of stiff structural natural composites are to provide protection, shape, and support and to serve as jointed limbs and weapons.

Synthetic composites, (i.e. combinations of two or more materials) were first constructed to provide higher levels of performance than a

monolithic material alone was able to supply. Early civilizations made use of rigid composite materials such as laminated bows employed for strength and straw and mud mixtures for building materials. They recognized that certain combinations of materials were synergistic for strength and toughness. In modern technology, the major attractions of synthetic structural composite materials are that they can be more resistant to high-temperature deformation, as well as lighter, stiffer, stronger, or tougher than their constituent single-component materials.

Rigid synthetic composites are composed of two or more constituents in a wide variety of configurations. Some of these are shown by classification in Figure 3-15. Similarly, in natural biological materials, many diverse examples exist of rigid composites. Examples discussed in Chapter 2 include wood (Figure 2-4), bone, and the nacreous structure of a mollusk shell (Figure 2-5).
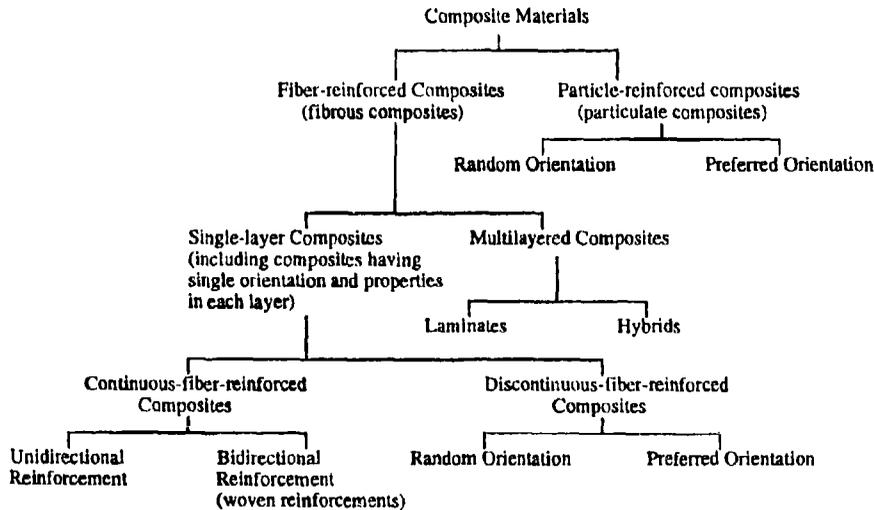
FIGURE 3-15 Classification methods for composites.

Elastic Response of Rigid Composite Materials

In order to compare the behavior of some biological materials to synthetic materials, it is useful to look at functions of simple shapes. For example, if the goal is to minimize weight for a given stiffness for the buckling of a slender column or a tube, a plot such as that shown in Figure 3-16 can be useful. In this case, one can compare constant lines of $\sqrt{E/\rho}$, where "E" is Young's modulus and "ρ" is density, for wood products, synthetic polymers, composites, ceramics, and metallic alloys.
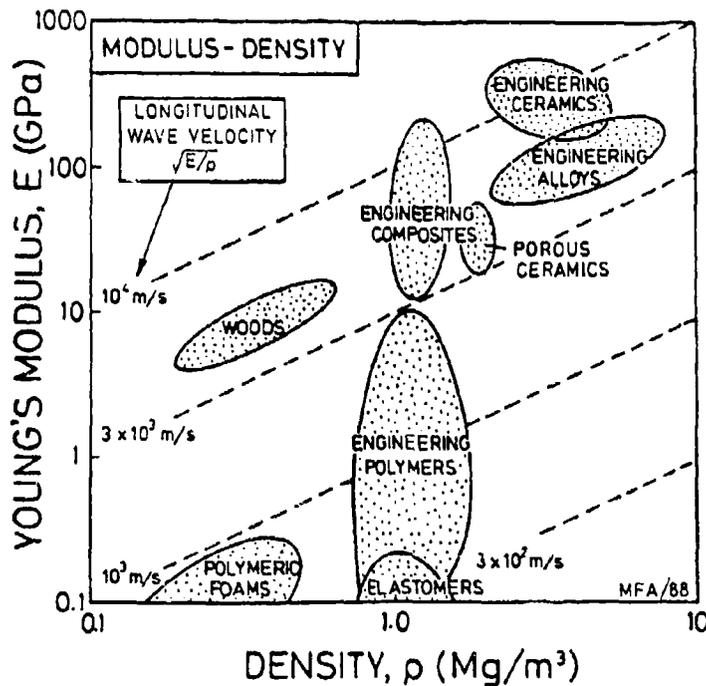
FIGURE 3-16 The idea of a materials property chart: Young's modulus, E, is plotted against the density, ρ, for classes of materials. Log scales allow the elastic wave velocity $v = (E/\rho)^{\frac{1}{2}}$ to be shown as parallel contours. Source: Reprinted from Acta Metallurgica, Volume 37, M. F. Ashby, On the Engineering Properties of Materials, Pp. 1273-1293, Copyright (1989) with kind permission from Elsevier Science, Ltd.

For a better part of three decades, wide use has been made of the rule of mixtures for the analysis of simple composites undergoing elastic strain, for both particulate-reinforced (Broutman and Krock, 1967; Jones, 1975) and fiber-reinforced (Kelly and Davies, 1965) materials and for laminates (Lee et al., 1991).

This rule describes the elastic behavior of a continuous fiber-reinforced composite as:

$$E_c = V_m E_m + V_F E_F \qquad (Eq. 3\text{-}2)$$

where:

E_c is the Young's modulus of the composite
E_m is the Young's modulus of the matrix material
V_m is the volume fraction of the matrix material
E_F is the Young's modulus of the fiber
V_F is the volume fraction of the fiber phase

In the case of discontinuous reinforced composites, mixing rules are significantly more complex. Reinforcement size, shape, and distribution influence the behavior of the composite. For example, for a relatively simple case of a dispersion of cubic particles, the elastic modulus of the composite is (Jones, 1975):

$$\frac{E_c}{E_m} = \frac{E_m + (E_p - E_m)\, V_p^{2/3}}{E_m + (E_p - E_m)V_p^{2/3}\,(1 - V_p^{1/3})} \qquad (Eq. 3\text{-}3)$$

where:

E_c, E_m and V_m are as above, and
E_p is the Young's modulus of the particle
V_p is the volume fraction of the particulate material

To account for directionality in laminates, two limiting cases that bound the elastic properties of two-phase composite systems are as shown in Figure 3-17.

a. Voigt Model
(equal strain)

b. Reuss Model
(equal stress)
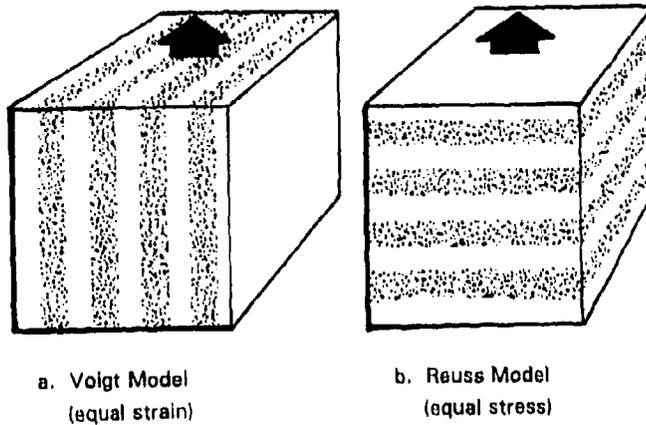
FIGURE 3-17: Limiting cases for composites: (a) equal strain (Voigt) model; (b) equal stress (Reuss) model.

The Voigt model (Eq. 3-4) is based on equal strain response in both constituents of the composite (Eq. 3-4 is essentially the same as Eq. 3-2). The Reuss model (Eq. 3-5) is based upon an equal stress condition in both phases.

$$E_c = V_F E_F + (1-V_F) E_m \qquad (Eq. \ 3\text{-}4)$$

$$\frac{1}{E_c} = \frac{V_F}{E_F} + \frac{(1-V_F)}{E_m} \qquad (Eq. \ 3\text{-}5)$$

The foregoing basic relations have also been applied extensively in structural biomaterials (see, e.g., Vincent, 1990). Ker (1977) modified the rule of mixtures relation for locust and beetle cuticles:

$$E_c = E_m (1-V_F) + E_F V_F (Z) \qquad (Eq.\ 3\text{-}6)$$

where Z is a factor which is a function of stiffness, area, radius, spacing, length of fibers, and the change in shear in the matrix caused by the presence of the fiber.

In a study of nacre (Jackson et al., 1988), a "shear lag" analysis by Padawer and Beecher (1970), which had been developed for platelet composites, provided a more complex relation for the modulus of the composite:

$$E_c = V_{pl} E_{pl} [1-\tanh (u)/u] + (1-V_{pl}) E_m \qquad (Eq.\ 3\text{-}7)$$

where:

E$_c$ is Young's modulus of the composite
$u = S\{M\ V_{pl}/[E_{pl} (1-V_{pl})]\}^{1/4}$
S is the aspect ratio of the nacre platelet
V$_{pl}$ is the volume fraction of the nacre platelet
E$_{pl}$ is the Young's modulus of the nacre platelet
M is the shear modulus of the matrix

This prediction and another shear lag model by Riley (1968) follow the trend of the actual mechanical behavior of nacre better than the predictions of the Voigt or Reuss models. However, additional refinement of the models is necessary.

Analyses are much more advanced for synthetic materials, especially for polymer-based composites such as carbon-fiber-reinforced polymers or Kevlar-fiber-reinforced polymers. For those materials, a variety of plates and shell structures, including laminates, have been addressed, and simple structural load responses for configurations from idealized orthotropic to anisotropic to antisymmetric cross-ply and antisymmetric angle-ply composite

systems have been predicted with a measure of success (Hull, 1981; Ashton, et al., 1969).

The foregoing discussion centered on predictions of elastic moduli for synthetic and natural materials. However, precautions should be noted. As noted earlier, the moduli of many rigid biomaterials are very different in the wet condition than in the dry state. An example, given by Vincent (1990) is of horn keratin, which has a matrix phase Young's modulus of 0.9 GPa with 40 percent water and 6.1 GPa in the dry state. Similar effects, though perhaps not as dramatic, are observed in synthetic resin-matrix composites that take up moisture.

Toughening Mechanisms for Rigid Composites

Examination of the mechanical behavior of both synthetic and natural composites generally shows higher levels of toughness and resistance to cracking in carefully designed composites than in monolithic materials (Clegg et al., 1990). Mechanisms for toughness improvements in ceramics and ceramic matrix composites have been described (Becher, 1991). Among the examples cited are crack pinning, crack deflection, crack bridging and pull-out by dispersed particles and elastic reinforcing phases and grains, stress-induced microcracking, stress-induced martensitic transformation, and plasticity in metallic binder and dispersed phases. It has been demonstrated that providing weak interfaces in laminated ceramics can increase the work required to propagate a crack by a factor of over 100. A rationale for crack blunting in composite materials was provided by Cook and Gordon (1964). The mechanism proposed is fairly widely accepted as being a major contributor to toughening of composites.

The fracture path in nacre (mother-of-pearl) shows evidence of crack blunting and diversion (Figure 3-18). The work of fracture is highly directional and is governed by crack stopping at interfaces, followed by crack diversion through delamination. The critical role of the thin matrix material between the ceramic (calcium carbonate) platelets making up simulated "brick wall" structure has been well established. The glue-like matrix, which is well bonded to the ceramic phase and is highly ductile, tough, and tenacious, is also complex in both hierarchy and function. Deformation and failure of the fibrillar structure of the matrix, the anchoring mechanism of the matrix to the ceramic platelets, the nature of the bonding between the

complex constituents of the matrix (proteins, chitin), and the roles of different morphological types of superstructures (layer-laminated, prismatic, cross-lamellar, etc.) all need to be studied more closely in order to arrive at directions for improvement of synthetic composites.
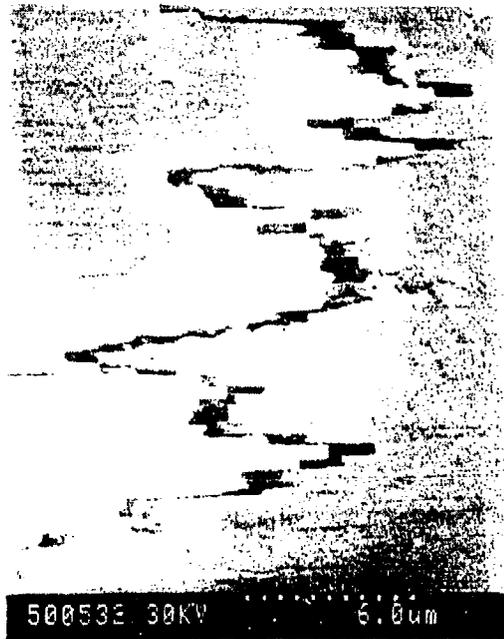
FIGURE 3-18 Fracture path through nacre. Source: Jackson et al., 1988.

Tough laminate composites having high resistance to crack propagation have been mentioned earlier. The fracture of these metallic composites and the fracture of nacre that is illustrated above are similar in the blunting of cracks by delamination at the interfaces of the dissimilar layers during impact testing.   If, however, interdiffusion occurs between layers in the metallic composite during processing, or if the bond strength is substantial, delamination may not occur, and the notch-impact properties will degrade. An example of a tough microstructure in a laminated composite of ultrahigh carbon steel and brass is shown in Figure 3-19.
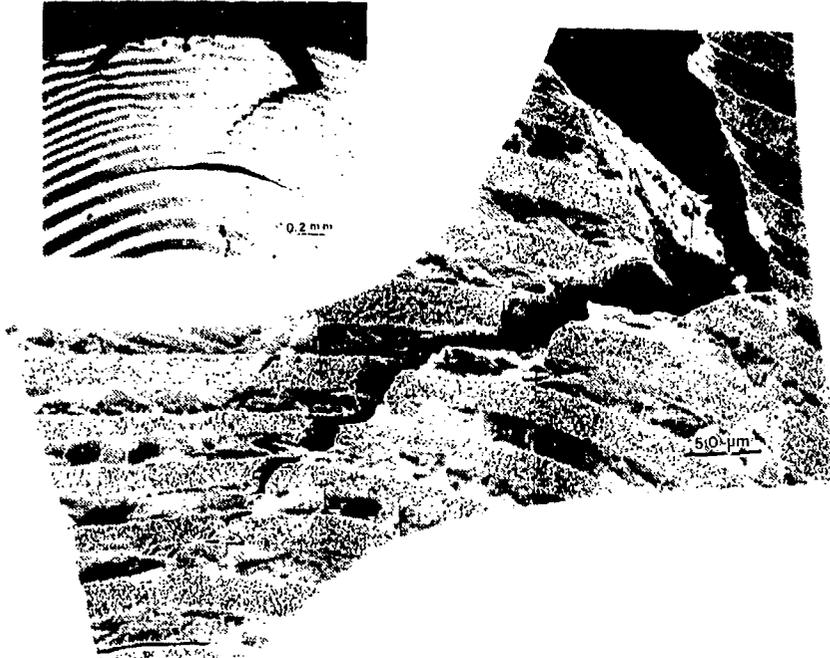
FIGURE 3-19 Crack propagation in an ultrahigh carbon steel brass 40-layer composite. Courtesy D. R. Lesuer, Lawrence Livermore National Laboratory.

In addition to crack blunting at interfaces, other energy-absorbing mechanisms can operate in both synthetic and natural composites. Shear yielding and microstructural defects that may create complex stress fields and deflect propagating cracks can be effective energy dissipators.

Strength Properties of Rigid Composites

Strength properties of composites are not so straightforward as are elastic properties. Although mixing rules have been shown to be valid in specific cases, for example, tungsten wires in a copper matrix (Kelly and Davies, 1965), they generally do not work well for prediction of composite strength in inorganic crystalline materials because of factors such as the strong dependence of strength upon grain size, the presence of residual stresses, crystallographic orientation, etc. (Chawla, 1987). Hull (1981) has described other

possible complications that relate to a variety of failures that may occur within the composite locally before the ultimate strength is attained.   For natural rigid composites that have a variety of reinforcements and matrices, and for adhesives, viscoelastic behavior adds other complications to strength predictions, as do factors such as nonlinear behavior of porous or cellular structures during deformation.

The determination of the strength of composite structures and the prediction of mechanical responses to complex service environments have been studied in some detail (NRC, 1991). The difficulty in the prediction and analysis of composite strength is compounded by the broad range of potential failure modes and operating environments. Composite failure modes tend to fit three broad categories: fiber-controlled failures, matrix- and interface- (or interphase-) controlled failures; or micro- and macro-instability failures. The dominant failure modes for composite structures include matrix cracking, delamination, tensile fiber failure, microbuckling, and global instability.   Also to be considered is the effect that service environmental factors such as moisture, temperature, chemical or electrochemical interactions, and radiation have in altering the mechanical properties and hence the mechanical response of the composite system.

Four factors have been identified that have hampered progress in the structural analysis of rigid synthetic composites and in the ability to predict failure events (NRC, 1991):

1.   implementation of design and analysis paradigms that neglect the effects of microstructural detail on the macroscopic response of composite materials;

2.   perception of the need to characterize fully the bewildering number of systems available;

3.   lack of consensus concerning failure modes and failure criteria; and

4.   persistent use of design and analysis paradigms that are based on metal technology.

The same general inhibitions apply in the case of natural composites While complex composite analyses have been undertaken, for example, on insect cuticle (Gunderson and Whitney, 1991, 1992),

they have resulted in limited success. A better understanding of the micromechanisms of deformation and failure in complex systems and of the application of analysis methods on multiple size scales is needed before additional progress is made in analytical mechanics and in the development of suitable analogues of such natural materials in synthetic composites.

4

FABRICATION OF HIERARCHICAL SYSTEMS

The benefits, in both function and performance, from the development of synthetic systems with hierarchical architecture have been illustrated in previous sections of this report. However, realization of this potential has been limited by available processing technology. The methods for precise control over all levels of structural arrangement simply are not available. While there are important lessors to be derived from studying how nature produces systems with precise control at all levels of hierarchy, the time scales involved in these processes would generally be prohibitive in synthetic fabrication. In order to be economical, synthetic processes need to be able to be accomplished at a much greater rate and scale.

Although the use of synthetic hierarchical concepts is at an early stage, many structural variables can be altered more readily in synthetic materials than in natural materials. The following variables can be altered (though, for the most part, not independently) through control of fabrication processes:

- elemental composition and structure (including tailored lattices);
- molecular structure;
- nanostructures and boundaries;
- dislocation and other defect structures;
- cells and other substructures (size, morphology, structure, orientation);

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- sizes, distributions, and morphologies of constituents and phases;
- grain sizes and morphologies;
- crystallographic orientation;
- orientation distributions;
- phase relations (including transformations);
- interfaces at all levels; and
- microstructure.

In this chapter, the present state of the art of fabrication technologies for synthetic hierarchical systems is discussed. Processes to produce many of the systems described in detail in Chapter 3 are outlined, with emphasis on the structural variables that can be affected through process controls.

Emerging and innovative processes or techniques to provide control of structural variables at multiple size scales or to enhance the ability to produce synthetic hierarchical systems are also discussed. For example, methods exist for production of multilayer ceramics (Otsuka, 1993) and for computer-aided modeling of parts from photo-polymerizable resin (Jacobs and Reid, 1992). These kinds of methods could provide organization down to the milli- and micro-scale. For organization on the nanoscale, self-assembly of the constituents would be necessary. For self-assembly processes, the component materials would need to be delivered to the appropriate sites via the gas phase or the liquid phase and could be in a molecular form, as a precursor or as a submicron particle. Positioning could be determined by masking or by photo-induced reactions. Direction of self-assembly might depend on additives that modify phase separation to favor particular sizes and shapes. Some of the processing methods can be borrowed from the semiconductor industry, but to form metals, polymers, and ceramics of many types, there is a need to extend the range of materials that can be deposited, especially where materials of different melting points, etc., are to be co-deposited.

Many methods are available or can be envisaged for the control of structures in films. Sequential application of these techniques, or the simple stacking and fusing of films, can be used to make three-

dimensional parts with a high degree of structural control. Many complex biological growth processes can also be viewed as a combination of a close control over a surface, plus progressive extension on the third dimension, to build up a solid body.

SYNTHETIC PROCESSING

Fiber Processing

Many of the advances in synthetic fiber property control of the past several decades originate from the separation of those processing steps involving orientation, crystallization, and "structural" perfection. For example, spinning polymer under conditions of low net chain orientation gives rise to point nucleated lamellar crystals, which emanate from the point with radial symmetry. Subsequent orientation of this spherulitic structure in the solid state (drawing) leads to a microfibrillar microstructure that is characterized by highly oriented noncrystalline chains, a crystalline lamellar thickness that reflects the stress-temperature history imparted by the draw process, and a structural retention of both the original entanglement network present in the polymer prior to crystallization and the interaction present in the spherulitic structure. The transformation of spherulitic structure during drawing has been treated in detail by Peterlin (1971, 1978, 1979, 1983), who suggested that the final structure is a microfibrillar hierarchy, with the size and connectivity of the hierarchical elements a function of the starting structure (see Figure 4-1). Fiber morphology induced in this fashion tends to show high orientation in both crystalline and noncrystalline regions. In most cases, the observation of drawn spherulitic structure shows only the 100 Å microfibrils.

If fibers are produced under spinning conditions that impart a net strain to the molecular chains prior to or during crystallization (i.e., conditions that lower the entropy of the ground state of the melt or solution), the morphology of the initial crystals produced is fibrillar rather than spherulitic. Depending on the nature of the starting
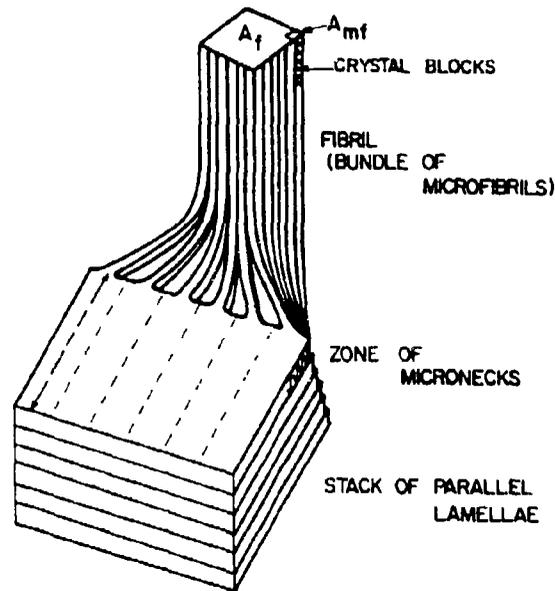
FIGURE 4-1 Schematic of cold drawing process with transformation of the lamellar texture into a microfibrillar structure. Source: Peterlin, 1972.

polymer and the time-temperature-stress profile of the spin line, the concentration of these fibrillar crystals (often referred to as line nuclei) varies from making up essentially all of the fiber microstructure to relatively few fibrils being formed. The concentration of fibrils is controlled by the stress imposed during spinning. In general, line-nucleated structures tend to be characterized by a high degree of preferred molecular orientation in crystalline regions and a lower degree of orientation in noncrystalline regions. In summary, it may be stated that low entropy starting states (high orientation) give rise to fibrillar crystals (line nuclei), while high entropy starting states (random coil) give rise to spherulitic crystals (point nuclei). Fiber processes that favor line nucleation offer the opportunity by separating the levels of orientation in the various structural elements to separate mechanical and thermal fiber performance.

An alternative to straightening flexible chains through the application of stress to the spin line is to start with a stiff, "rod-like" molecule. Such molecules tend to be nematic liquid crystals, examples of which are the lyotropic poly(p-phenylene-terephthalamide; Kevlar™) and the thermotropic copolyesters (Vectra™). Such molecules have little tendency to chain fold and show highly fibrillar, hierarchical microstructure in the solid state (Sawyer and Jaffe, 1986), as shown in Figure 4-2. While the existence of a fibrillar hierarchy in liquid crystalline polymer fibers has been established, it remains unclear what the origin of the hierarchical elements are. Possibilities include "crystallization," reflection of previously generated entanglement network, or the fracture of larger-diameter species during processing.

All oriented polymers and all synthetic fibers are characterized by a microfibrillar morphology with a diameter of about 100 Å. While the origin of this structure is qualitatively understood, quantitative understanding of its formation is lacking. The relationship of the elements of the hierarchy to fiber properties is reasonably in hand, with properties that are predicted from mechanical models correlating well with measured data (mostly axial mechanical performance). What is missing are the quantitative theories and models necessary to relate fiber formation conditions to microfibrillar (hierarchical) detail.

In conclusion, a fundamental difference in the driving forces that control the formation of fibrillar hierarchies in natural and synthetic fibers should be noted. In nature, the origin of level and size of hierarchical structure is primarily driven by chemistry (specific interchain and intrachain interactions). In contrast, structure formation in synthetic systems is driven by physics, which leads to less defined structures, which are often better described by size distributions than single size parameters. Hence the appearance of hierarchy in nature is "by design" to satisfy a given performance need, while synthetic polymer hierarchies are not present through the designing of structure for performance but rather because of underlying process physics criteria, the impacts of which are often not
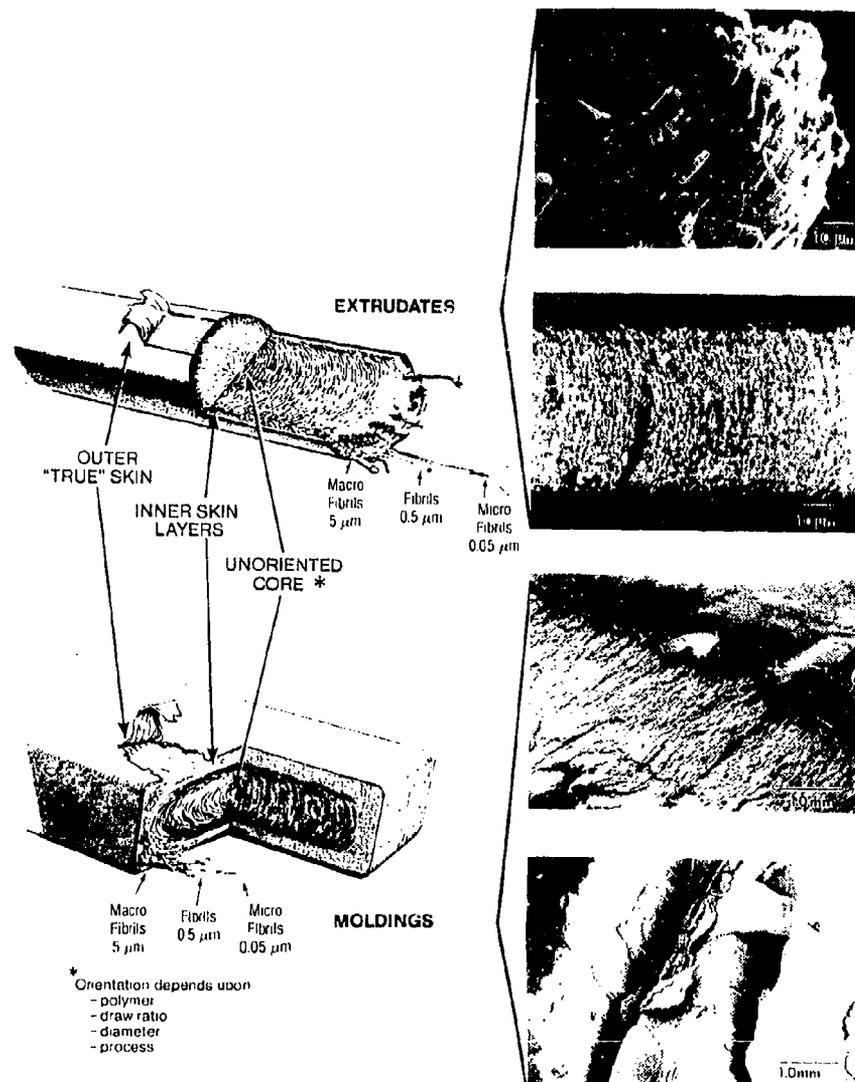
FIGURE 4-2 LCP polymer structure model of extrudate and molding. Source: Sawyer and Jaffe, 1986.

fully appreciated. A significant opportunity therefore exists to learn from natural systems to produce the next level of sophistication in synthetic fiber products.

Multilayer Processing

An obvious way to build a complex hierarchical structure is to construct it as a series of layers. Multilayer processing includes lamination of structural composites, polymer coextrusion, and step-wise deposition processes.

Based on design criteria derived from nacre, as discussed in Chapter 3, the processing of ceramic/metal and ceramic/polymer laminated composites through tape casting and liquid infiltration techniques, specifically with boron carbide/aluminum and boron carbide/polymer composites, respectively, has been accomplished. These laminated composites can be formed by one of three basic methods: (1) partially sintered ceramic tapes are sandwiched with metal or polymer sheets and then heated to induce infiltration of the metal or the polymer; (2) nonsintered ceramic tapes are stacked, partially sintered, and then infiltrated with metal or polymer; and (3) nonsintered ceramic tapes of different porosity are laminated (stacked and pressed), partially sintered, and then infiltrated. In these cases, the resulting structure is a ceramic/metal or ceramic/polymer laminated composite with metal or polymer at intra- and interlayers.

The reinforcement content of laminated samples is altered by changing the ratio between the matrix-rich and boron carbide-rich layers in the microstructure. The effect of changing the thickness of the laminae on both fracture strength and fracture toughness is in agreement with the Hall-Petch relation (Eq. 3-1). The coarsening of the microstructure by increasing the tape thicknesses degrades the mechanical properties to values approaching those for isotropic samples. Structures with more-finely graded laminates have not been processed at this time because of the difficulty in casting and handling tapes thinner than 15 nm. Attempts to form ultrafine laminated layers

in hard and soft steel sandwich composites by deformation processing resulted in break-up of the layers.

An inexpensive method for producing laminated plastic films directly through coextrusion of two or more polymers has shown great flexibility (Alfrey and Schrenk, 1980). The coextrusion process, shown schematically in Figure 4-3, consists of introducing molten parallel streams of polymer through feed ports and passing them through a die to produce a thin, wide sheet. To maintain the parallel orientation of polymer layers, the transition region from the feed stream through the die is particularly important. Complex polymer films are commonly extruded with five or more layers in order to provide barriers to permeation of different gases in food packaging. Baer and co-workers have shown that novel properties can be induced in polymer sheets made by coextruding two polymers as hundreds of very thin alternating layers of, for instance, soft and hard polymers (Ma et al., 1990a, b). This polymeric "millefeuille" structure could be extended to more-complex arrangements and more than two polymers to make a hierarchical structure. The final film properties depend on the constituent polymer properties, the layer thicknesses, and the nature of the interfaces between layers.

The last twenty years have seen the development of a battery of techniques for depositing materials in thin layers from the vapor phase. These include sputtering, chemical-vapor deposition, and molecular-beam epitaxy (Dresselhaus, 1987; Sinjo and Takada, 1987). The resulting films can be a few atomic layers thick and can be patterned down to a scale of a few microns. Vapor phase methods will probably always be preferred for thin films, but for layers of 100 nm or more, it is also sensible to utilize methods of deposition from liquid solution or suspension. Methods that could be applied to the buildup of patterned-layer structures include photopolymerization, electropolymerization, epitaxial crystallization on modified surfaces, metalorganic deposition, localized particle attachment, Langmuir film deposition, and standard casting or coating methods. In combination, these methods could be used to process complex composites that contain a wide range of organic and inorganic materials.
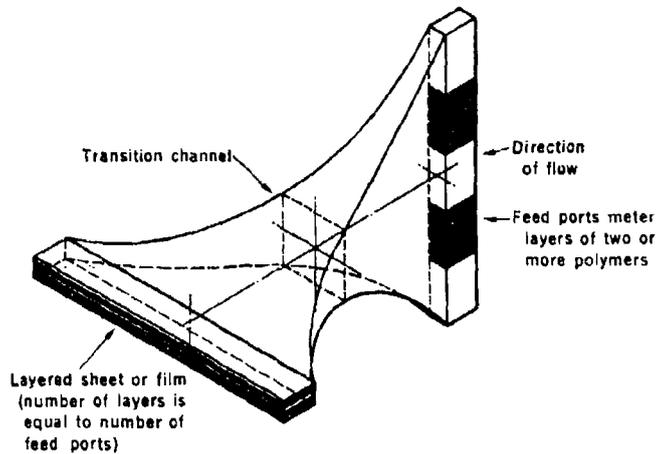
FIGURE 4-3 Schematic diagram of the feedblock method of coextruding multilayer polymer sheets and films. Source: Alfrey and Schrenk, 1980.

The formation of polymeric and composite materials in biology is an excellent example of control of structure. However, the constituents of biological materials have been limited to organic polymers plus phosphates, silica, iron oxides, and carbonates. Current work is extending the principle of in situ precipitation to other oxide ceramics, metals, and sulfides (Calvert and Mann, 1988; Calvert, 1994). Related efforts are developing the ability to locally deposit minerals from solution on patterned surfaces (Rieke et al., 1993). This promises to permit complex structures to be built up by a series of precipitations, in the same way that integrated circuit technology allows complex structures to be built on a silicon wafer. However, deposition from aqueous solutions at room temperature will permit a much wider range of materials to be incorporated into the structures.

Injection Molding

Sequential growth of complex structures requires revolutionary approaches to manufacturing and cannot be expected to make a major

impact in the short term. An important direction for immediate application to production of hierarchical structures is by more-sophisticated molding processes.

Progressive refinements in plastic molding methods, including injection molding and extrusion, have allowed complex blends of materials to be formed directly. Also, injection molding of reinforced polymers and reinforced reaction injection molding have allowed higher fiber contents and longer fibers to be introduced into larger parts while still retaining the advantages of mass production.

An example of structural hierarchy that results from molding processes is the injection molding of a liquid crystal polymer (LCP; Weng et al., 1989). The previous section discussed how one-dimensional hierarchy is introduced in liquid crystal polymer fibers through flow orientation. Similarly, injection molding of a liquid crystal polymer or a reinforced composite results in a graded structure, with high preferred orientation in the direction of flow (mold filling direction) near the mold walls and decreasing orientation toward the part interior. A schematic of this graded structure is shown in Figure 4-4. The properties of the molded parts can be influenced when the part and mold are designed by controlling the flow parameters within the mold through placement of gates and risers.

One-dimensional hierarchies can be introduced by complex film dies, by building up stacks of polymers during extrusion, or by fusing a series of films during a rolling step. It is intrinsically quite feasible to construct a similar two-dimensional arrangement into an extruded rod or pipe. For instance, reinforcing threads could be coextruded with a tough matrix, and could be spirally arranged, to form pipe.

Such coextrusion of polymers is standard procedure. Short reinforcing fibers can be blended into the polymer, but there is little control over their orientation or local concentration. Finer reinforcements with better axial ratios are available, but it is not yet possible to reinforce on the same scale as is seen for the mineral in bone. Ceramic, glass, and metal reinforcements could be added by in situ reaction (with orientation control by applied electric field or currents, etc.), which might offer more control than simple additions of fibers or flakes.

a. LCP matrix　　　　　　　　b. LCP composite
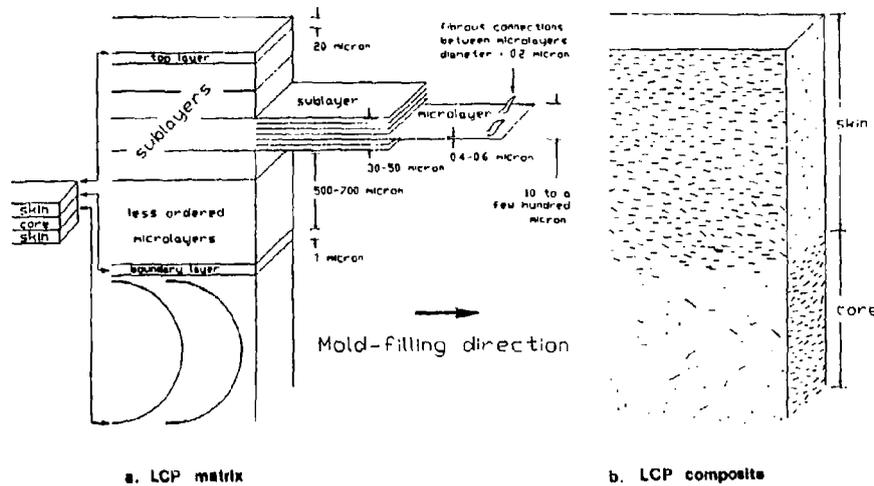
FIGURE 4-4 Proposed hierarchical model of injection-molded (a) unreinforced liquid-crystal-polymer resin material and (b) its short-fiber reinforced composite. Source: Reprinted from Weng et al., 1989, p. 278 by courtesy of Marcel Dekker, Inc.

Thus, many already available molded materials are hierarchies. An analysis of the advantages to be gained from flexible structural control, coupled with a broad approach to the manufacture of multimaterial composites, is required.

Three-Dimensional Manufacturing

Self-assembly directed by highly structured copolymers can be expected to yield controlled fine structures on the scale of 10–100 nm. For example, block copolymers can promote fine-scale mixing in polymer blends, since the copolymer may be required, as a consequence of its structure, to remain at an interface. At larger scales, the required hierarchy must be processed directly.

A number of research efforts involving layer-wise syntheses of complex structures are underway. These efforts resemble mineralization in large biological structures in which minerals are

deposited by chemical precipitation at a "moving front" that passes through the bone or shell matrix. The uniquely high volume fraction of mineral phase that is attainable in biological composites and the local variations in properties are due to this strategy.

Such methods are known as rapid prototyping or free-form manufacturing and have recently received much attention. Polymer parts are prepared by laser photopolymerization in a layer of monomer at the surface of a part. The laser is computer driven to produce the required cross-section in each successive layer. As a result, a prototype can be rapidly produced from a computed design. Variations of this process are being developed for ceramic powder deposition by local fusion of polymer-bound particles (Marcus and Bourell, 1993) and by patterned deposition of slurries that uses an ink-jet printer (Sachs et al., 1992). It is already a common practice to make ceramic packages for microelectronics by sintering a stack of shaped green sheets. It is clearly a small step to depositing each layer from a slurry rather than from a pre-cast soft sheet. By carrying out the chemistry necessary for ceramic particle formation or polymer deposition on each layer in turn, and by using lithographic methods to pattern each layer, complex hierarchical structures can be built up.

BIOLOGICALLY INSPIRED PROCESSING

The growth of biotechnology is opening the way to the use of biological processing for the manufacture of materials. In polymers, it appears likely that cellular synthesis of artificial proteins or polysaccharide will be possible. These macromolecules should be capable of self-assembly into higher-order structures by reason of the detailed sequence of units on the chain. However, at present, biological synthesis and processing are far from completely understood. The following paragraphs describe several aspects of biological synthesis and processing that appear to offer prospects for new developments in materials technology.

Macromolecular Synthesis

Production of hierarchical materials requires synthesis of the constituent molecular—and more often macromolecular—species. Organic composites, for example, consist of polymeric matrices and either particulate or fibrous reinforcing materials, and laminates are generally formulated from preformed polymers. In each case, production of these constituent materials requires relatively advanced manufacturing technology in order to ensure control and repeatability of critical molecular parameters such as length, composition, stereochemistry, branching, and cross-linking of the polymer chain.

The present state of the art of macromolecular synthesis is such that these critical molecular parameters are indeed subject to control, but only in a statistical sense. For example, existing synthetic methodologies allow the preparation of polymeric materials characterized by well-defined and predictable *distributions* of molecular weights but cannot afford chain populations of *uniform* molecular weight. Similar statements hold for the other important molecular parameters. Molecular heterogeneity is important in optimizing polymer processing characteristics (e.g., melt viscosity) while maintaining acceptable mechanical and thermal characteristics. However, it is not yet clear whether aspects of biological structures, such as self-assembly, can be reproduced without going to synthetic methods that require full control of the sequence of units on a polymer chain.

Biosynthetic Routes to New Polymeric Materials

As outlined above, conventional approaches to the synthesis of polymers lead to populations of chains characterized by relatively broad distributions of length, composition, stereochemistry, etc. In contrast, the structural proteins of higher animals (e.g., silk, collagen, and elastin) are synthesized under direct genetic control and are, as a result, essentially uniform in chemical structure. Because natural

hierarchical architectures emerge from complex—and as yet poorly understood—processes of molecular assembly, a high premium is placed in nature on precise control of macromolecular structure. Full exploitation of such assembly processes in the creation of new synthetic materials will require similar control and should stimulate exploration of new routes to polymers of well-defined structure.

Perhaps the most straightforward approach to this problem is to adapt directly the chemistry of protein biosynthesis to the creation of new artificial proteins with useful structural properties. Several successful reports on this approach have appeared (Capello et al., 1990a; Creel et al., 1991), and it seems likely that general strategies for genetic engineering of new structural materials will emerge rapidly. Indeed, attention is already shifting from biological problems (e.g., the stabilities of artificial genes and proteins in microorganisms) associated with synthesis to the engineering of the physical (Tirrell et al., 1991) or functional (Cappello and McGrath, 1994) properties of the product polymers.

Biological syntheses of other classes of polymers are also growing in importance. Poly(β-hydroxyalkanoate)s (Doi, 1990), cellulose (Johnson et al., 1989; Ben-Bassat et al., 1986) and a wide variety of enzymes and chemical intermediates are now being made in substantial quantity by microbial fermentation. In vitro enzymatic catalysis of polymerization is also being pursued (Wallace and Morrow, 1989).

Processing of Biological Polymers

Most synthetic polymers are processed by melting followed by extrusion or molding. One intriguing aspect of biological polymers is the fact that insoluble materials can be formed in an organized fashion at room temperature. This implies some way of manipulating the material in a temporarily soluble form. This could become an important component of processing for complex hierarchical materials where fine-scale control is the essence. The synthesis and assembly of

silk fibers provide excellent examples of the kinds of biological materials processing that merit increased attention from the materials community.

Silks are produced by a variety of organisms, including the domesticated silkworm (*Bombyx mori*) and orb-weaving spiders. Silks from these organisms are characterized by an antiparallel beta sheet secondary structure stabilized by hydrophobic and hydrogen bonding. Some of the fibers made up of silk polypeptide are characterized by a combination of high strength and high extensibility. Some silk polypeptide are high molecular weight, over 300 kilodaltons in the case of major ampullate gland silk, which forms dragline silk, or the strongest of the silks produced by most orb-weaving spiders.

In the silkworm, and presumably in spiders, the polypeptide is synthesized and exported from epithelial cells that line the lumen of the posterior region of the major ampullate gland (Fossey et al., 1991; Fraser and MacRae, 1973). After synthesis and export into the lumen of the posterior region of the gland, the polypeptide moves to the middle portion of the gland for storage. Here, the polypeptide is at a concentration of about 20 percent, the viscosity is high, the shear rate is low and the pH is in the 5.6 to 5.0 range. After passing into the anterior region of the silk gland, the protein concentration rises to around 30 percent, viscosity is again low despite the higher protein content, and the pH drops to below 5.0. During the latter process, and as the polypeptide is spun into air through the spinneret into the final silk fiber, the beta sheet conformation is realized, and an insoluble fiber is formed (Kerkam et al., 1991).

The mechanisms involved in this natural system for processing polypeptide in an aqueous environment at ambient temperatures are of interest. The result of this process is insoluble fibers with unusually high tensile strength and global alignment. The properties of birefringence and relatively low viscosity at high concentrations of polypeptide are characteristic of these materials during this processing.

Structural Polysaccharide: Chitin, Chitosan, and Celluose

The polysaccharide, chitin, is associated with naturally occurring composites such as cell walls of filamentary fungi and insect and crustacean exoskeletons. Electron micrographs taken of cuticle-secreting cells of the locust indicate that chitin synthesis occurs at the cell surface. Coupled polymerization and assembly (crystallization) processes occur, as with cellulose, although the details of this process are not understood. Studies with fungal preparations have demonstrated that chitosan fibers can be formed in vitro (Ruiz-Herrera and Bartn.cki-Garcia, 1974). It is generally accepted that in vivo assembly of chitin and chitosan fibers involves the tandem action of a series of enzymes. Based on the insolubility of chitin, it is also presumed that assembly occurs in association with the cell wall. Two enzymes, chitin synthase (membrane bound) and chitin deacetylase (soluble), are key to the polymerization of the N-acetylglucosamine monomers into chitin followed by deacetylation to form chitosan. The deacetylase is inactive against crystalline chitin, and tightly coupled polymerization and assembly processes are also seen in the fungal system.

Cellulose, the most abundant polysaccharide in nature, is produced by plants and bacteria. Cellulose-producing bacteria include the genera *Acetobacter*, *Rhizobium*, *Agrobacterium*, and *Sarcina*. Most of the clues to cellulose biosynthesis and assembly are derived from studies on bacterial systems, since cellulose is synthesized and assembled independently from other polysaccharide and matrix components.

Cellulose biosynthesis in bacteria couples synthesis with assembly; otherwise a random disorganized fibrous matrix would be expected. Instead, a highly crystalline fibril structure is formed at the cell surface. A single bacterial cell can incorporate up to 200,000 glucose monomers per second into a growing cellulose polymer chain. The final assembly step involves the formation of a ribbon of fibrils with about 1,000 glucan chains. The cellulose synthase complexes are localized in aggregates at the cell surface to assure rapid and ordered assembly into larger microfibril at the sites of synthesis.

Self-assembly processes are involved that are indirectly controlled by the polymerization steps and the morphology of the cell (ordered-granule hypothesis; Ross et al., 1991). In plants and algae, analogous steps related to synthesis and assembly are indicated.

A process to produce bacterial (*A.xylinum*) cellulose as a fine, continuous, cross-linked network instead of separate fibers has recently been developed (Ben-Bessat et al., 1986). The small diameter (0.1 to 0.2 μm versus fibers with diameter of 30 μm that are produced from wood pulp), coupled with the network structure, provide improved surface area for a number of potential applications where high water-holding capacity is critical.

Self Assembly

An impressive feature of biological materials is that the structure is well engineered on length scales from microscopic ($\sim$1 nm) up to macroscopic dimensions ($>$1,000 nm). Nature appears to be adept at "processing" in the difficult intermediate (mesoscopic) length-scale regime of 10–100 nm. A method employed to great advantage in nature is based on the split-chemical tendencies of surfactant molecules, that is, amphiphilic preference for interfaces between hydrophilic and hydrophobic regions. Recognized as the "self-driven" mechanism for assembly of lamellar-bilayer membranes, amphiphilic characteristics lead to other mesoscopic architectures (e.g., cubic, hexagonal, biocontinuous, subtypes of lamellar structures, etc.). In association with other cosurfactants, these systems create three-dimensional lattices, lamellar arrays, and hexagonal stacks of "tubes," all with spatial periods of tens of nanometers. These special features of lyotropic mesophases expose a potential for use as structural "templates" in preprocessing of hard materials. thereby extending control of the microstructure to much larger dimensions. Possible applications range from presintering processes for ceramics and ceramic catalysts to fabrication of intercalated composites.

From the viewpoint of industrial processing, the immediate concern will be cost: biologically derived surfactants are expensive.

However, the physical–chemical mechanisms that drive the phase behavior are beginning to be understood and can be reproduced with synthetic diblock copolymers to achieve similar mesophases. These synthetic amphiphiles will be especially useful in processes where the chemical and physical conditions are harsh.

Vesicle Mediated Multicomponent Processing

Intravesicular precipitation of inorganic, crystalline particles is common in nature. Nanometer-sized magnetite particles, for example, are fabricated in intracellular vesicles by certain types of bacteria that have precise control over particle morphology and orientation (Frankel and Blakemore, 1984). In addition, single component particles can be precipitated within synthetic vesicles as a model system for the study of biomineralization (Mann and Williams, 1983; Mann and Hannington, 1988).

Particle precipitation within vesicles has several fundamental differences from bulk precipitation methods due to the unique properties of the lipid bilayer. In addition to forming a reaction cell that limits particle size, the bilayer serves as a semipermeable membrane to ion diffusion. Generally, phospholipid vesicles are nearly impermeable to cations, with typical permeability coefficients between 10^{-12} to 10^{-14} cm/s (Johnson and Bangham, 1969; Hauser et al., 1972; Papahadjopoulos, 1971). Diffusion rates of anions, on the other hand, are significantly higher than for cations (Bangham et al., 1965), but are still low (10^{-10} cm/s for Cl^-). This characteristic produces a system in which cations are essentially "trapped" within the phospholipid cage until precipitation can occur (Mann et al., 1986). This could enhance chemical homogeneity within the system and facilitate the aqueous precipitation of water--soluble phases (such as $Ba(OH)_2$). Figure 4-5 shows a typical transmission electron micrograph of the vesicle-formed particles using the yttrium, barium, copper, and silver nitrate precursors. The particle size is smaller than the corresponding vesicle size.
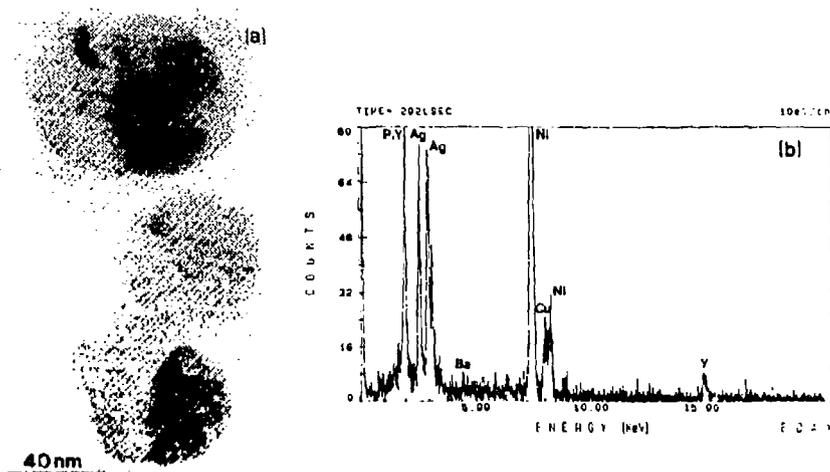
FIGURE 4-5 (a) Transmission electron micrograph of multicomponent particle formed within vesicle and (b) energy dispersive spectra of single particle. Source: Liu et al., 1991.

In summary, this biomimetic system is truly multifunctional in that it simultaneously acts as: (1) a reaction cell for particle precipitation, (2) an ion selective membrane that affects precipitation kinetics, (3) a barrier to prevent spontaneous agglomeration of the ultrafine particles, and (4) a lubricant/dispersant that facilitates particle rearrangement during particle consolidation.

Cell Seeding

Cell seeding, or cell transplantation, for ie development of specific tissues in vitro or in vivo, has become a highly attractive and exciting prospect. The general protocol that is envisaged is the isolation of cells with the potential for specific phenotype, which may then be incorporated into a support matrix and finally be transplanted as an in vitro-generated replacement tissue in a patient. The motivation for this approach in the medical community is the

application of these engineered tissues for use as biological grafts to replace diseased, damaged, or aged parts that cannot be replaced easily or satisfactorily with man-made materials. This can cover a range of applications, from the improvement of current treatment modalities to the opportunity of offering life-saving therapy. Cell-matrix transplantation appears to be particularly attractive for the replacement of tissues such as skin and cartilage.

Skin is the largest organ of the body, and although the body has developed highly efficient mechanisms to repair skin, major events of trauma and surgery can often require skin grafting. The availability of in vitro–generated skin could offer life-saving treatment to many patients (for example, burn victims with little remaining skin). Skin is a highly organized and differentiated tissue, but careful basic science studies have developed this technology into an example of success for in vitro–generated tissues. A successful system has been developed for the production of a type of skin in vitro that appears to result in a well-differentiated tissue and that has the potential to be clinically usable. There appears to be enormous potential for the application of in vitro–generated tissues seeded with cells. Recent scientific and technological advances make this a topic with achievable goals rather than an idealized hypothesis.

5

CONCLUSIONS AND RECOMMENDATIONS: SCIENTIFIC AND TECHNOLOGICAL OPPORTUNITIES

Biological structures are characterized by hierarchical architectural designs in which organization is controlled on length scales that range from the molecular to the macroscopic. These materials are multifunctional and are produced in situ at room temperature and atmospheric pressure. Many such structures are self-healing and remarkably durable, and many display properties that change in response to a changing environment; features of biological materials that represent desirable, and as yet unattainable, objectives in the design and manufacture of synthetic materials systems. Nature is parsimonious in its use of constituent materials, it returns to these same materials again and again to realize an astonishing range of structure and function.

The utility of many synthetic hierarchical materials is limited at the present time by shortcomings in fabrication technology and resultant finished-part costs that are high. This is especially true for very high performance materials, that is, continuous fiber-reinforced composites (polymer, ceramic, metal matrix, etc.), materials designated for use under environmental extremes, and parts that need to function reliably for extended time periods. Similarly, there is always a need for more-efficient and more-sophisticated system designs, for applications ranging from improved performance aircraft and spacecraft to faster switching communication devices.

The Committee on Synthetic Hierarchical Structures concludes that the study of biological materials will provide many lessons for use in the development of new materials technologies. In some instances, this may take the form of direct utilization of biological materials or biosynthetic pathways; in other circumstances, biology will provide inspiration for the creation of new designs and new methods of fabrication. Some preliminary successes of this kind are described in chapters 3 and 4 of this report. The analysis of lessons learned from natural material systems could lead to the development of new classes of synthetic materials, improved processing technology, and innovative design and analysis approaches.

MATERIALS

The hierarchical architectures of biological materials systems rely on critical interfaces that link structural elements of disparate scale. The study of such systems reveals extraordinary combinations of performance properties, as well as limitations due to the modest thermal and chemical stabilities of biological molecules. Application of hierarchical design concepts to more-robust synthetic building blocks provides promising routes to high-performance adhesives and composites, biomedical materials, highly specific membrane and filtration systems, low-friction bearings, and wear-resistant joints.

Specific opportunities and needs for materials development that were identified in previous chapters include:

- synthetic constituents to produce hierarchical materials with useful performance over a broad range of environmental conditions;
- low-friction and wear-resistant materials for joints and bearings;

- adhesives that mimic the tenacity and toughness of biological adhesives; and
- composites with high volume fractions of reinforcements.

PROCESSING

Biological structures are fabricated via highly coupled, often concurrent, synthesis and assembly. In the conception and evaluation of synthetic and processing schemes for new materials systems, the prospects for integrated system fabrication should be carefully considered.

Specific needs to realize the full promise of integrated fabrication methods include:

- concurrent materials synthesis and structural assembly;
- processes to fabricate highly specific synthetic membranes and filters;
- use of cells to synthesize and deposit materials;
- biosynthetic pathways to the cost-effective manufacturing of new classes of shaped hybrid composites; and
- biosynthetic concepts and materials for self-repair of critical components and devices.

DESIGN AND ANALYSIS

Biological structures perform as parts of integrated systems and undergo continuous evaluation and refinement based on system performance. In analogous fashion, considerations of integrated systems design and performance will take on increasing importance in the

high-technology materials-related industries of the future. Interdisciplinary teams of scientists and engineers will be required to effectively design and develop structural systems with such complex architectures. The committee recommends that the academic and industrial sectors of the materials community prepare for this development through implementation of appropriate educational and engineering programs that are based on systems concepts.

Several universities have recognized the promise of this approach and have developed programs to address these needs. Although, due to the diversity of the field, bioengineering curricula may vary in detail, they all strive to bring together the biologists' knowledge of physiology, anatomy, biochemistry, and molecular biology with the engineers' knowledge of design and structure (Watanabe, 1993).

Lessons to be learned from the design of natural systems include:

- strong, durable interfaces between hard and soft structural components;
- tribological joints with low friction coefficients and remarkable durability;
- mechanistic understanding and analysis methods for deformation and failure of complex systems;
- energy-absorbing mechanisms of rigid biological composites;
- platelet and surrounded plate analytical concepts; and
- moisture-friendly synthetic systems.

SCIENTIFIC OPPORTUNITIES

The hierarchical structures observed in biological systems represent potential solutions to the problems of materials choice,

materials fabrication, and component or system design that are currently limiting the utility and implementation of many modern materials and design concepts. Although the prospects for new biologically inspired materials technologies are real, full exploitation of this approach will require advances in engineering, education, and enabling science. *Although there is a broad range of technologies that may contribute to the understanding of biomaterials, the committee recommends concentration on developments in structural biology, interface science, synthetic methodology, instrumentation, modeling, and theory to enhance the development and applications of hierarchical systems that are based on natural analogues.* Some instances in which the translation of hierarchical structures found naturally might significantly impact materials science and technology are described below.

Synthetic Methodology

As discussed in Chapter 3, the design and preparation of hierarchical materials will place a new premium on the synthesis of macromolecules of precisely defined primary structure and complex chemical composition. At present, the only methodology available for the preparation of such polymers involves the use of gene synthesis and recombinant-DNA technology to create artificial structural proteins. This methodology is powerful and may lead not only to the creation of polymeric materials with functions not obtainable through conventional synthetic methods but also to an understanding of how control of molecular structure and function can improve materials performance. However, it is clear that the thermal and hydrolytic sensitivities of proteinaceous materials will limit their applicability in many important synthetic materials applications. Generalization of the methods of controlled synthesis to new classes of monomers thus becomes an important objective.

Some initial developments along these lines may be foreseen. It has been known for many years that certain analogues of the natural amino acids can be incorporated into bacterial proteins with high

fidelity (Cowie and Cohen, 1957), and it is likely that additional examples will continue to be identified. As further information becomes available regarding the mechanisms of transfer RNA charging and proofreading, the rational design of amino acid analogues useful in protein biosynthesis can be anticipated.

Some first steps toward templated polymerization of other monomers have also been reported. Schultz and coworkers (Noren et al., 1989) have recently described a method whereby suppressor transfer RNAs that are chemically acylated serve to deliver unnatural amino acids to messenger RNA templates in an in vitro translation system. In this initial report, the method succeeded for α-amino acid analogues but failed when applied to β-amino acids. Despite this limited success, such methods offer a basis for systematic studies of templated polymerization processes. Progress in this area must be accompanied by advances in cell-free translation methodology if any impact on materials synthesis is to be made, since current cell-free methods are limited to the preparation of submilligram quantities of material.

Looking beyond templated polymerizations, one sees little current evidence of real progress toward efficient synthesis of genuinely uniform chain populations. Nevertheless, recent advances in living ionic and metathesis polymerizations have been substantial and may in time lead to higher-order control of chain length, sequence, and stereochemistry. Issues such as environmental impact of the manufacture and disposal of polymers, along with the need for continuing improvement of cost/performance within the polymer industry, will cause polymer science to move in directions that will tend to minimize the numbers of monomers (raw materials) utilized by the industry and hence reduce the number of the chemistries presently in the waste stream. To achieve this, while preserving or expanding the current product diversity available with commercial polymers, increased interest in the effects of synthetic polymer primary specificity of structure of synthetic polymers on cost and performance will be manifest.

Cellular Synthesis of Materials

It should be possible to develop cell "epitaxy" methods whereby biological cells are employed to fabricate thin layers (of organics or minerals) on synthetic material substrates, perhaps providing persistent maintenance and regulation as "epidermis." The objective is to use organisms as "microengineers" for structuring materials on difficult-to-manage length scales and with difficult-to-synthesize chemistries. The cellular mechanism is capable of organizing fibrous networks, for instance, with functional hydrogel components to produce low-friction, durable, fatigue-resistant joint bearings. Cellular responses to environmental effectors such as mechanical stress or hormones can beneficially change the composition and assembly of these materials. This is enabled through the coupling of specific protein synthesis and degradation with the constant monitoring of mechanical function and the state of need of the organism. Long-term cellular activity within the material can enable the repair of the material upon damage by reactivation of matrix formation. Not only could these advances create new membrane and biomaterial technologies but also new insights for structuring hard materials.

Rigid Structural Composites

Many of the rigid structural materials found in nature are composites that make up unusual compositions and configurations. For example, the nacreous material in mollusk shell is a segmented composite with a very low volume fraction of matrix phase in very thin layers. The ability to design and fabricate synthetic structures with similar characteristics, as well as the ability to mimic adhesion between the phases, could lead to composites with remarkable properties, by combining outstanding strength and stiffness with improved fracture toughness compared with that of monolithic materials. In addition to practical and cost-effective fabrication techniques, an understanding of deformation mechanisms and the

ability to optimize composite structures through mechanical modeling
are critical to the successful development of such materials.

Adhesives and Interfaces

Adhesives and interfaces play important roles in both synthetic
and natural composites. Although much has been done in adhesion
science and technology, there are opportunities to tailor new synthetic
adhesives and unique structural architectures through mimicry of
natural systems. Adhesives play a critical role in the formation,
strength, and durability of composite materials as agents responsible
for bonding between matrix and reinforcing phases. Advances in
composites have emphasized the need for durable adhesives that would
work in wet environments. Adhesives produced by organisms,
especially marine organisms, suggest themselves as candidates for
study, because they cure in the presence of water and resist its
subversive effects.

Naturally occurring marine adhesives are analogous to composite
thermosets in that they are made up of fiber, filler, and catalyst
molecules dispersed in a cross-linked resin. Resin proteins display a
regular, repetitive structure that is thought to be related to their
function (Waite, 1990). For example, the East Coast blue mussel
(*Mytilus edulis*) uses a resin polymer made up of approximately 80
repeats of a decamer. The West Coast mussel (*Mytilus californianus*)
has evolved in an environment with greater wave action than the East
Coast mussel and has resin virtually identical in structure except that
two residues have been interchanged and a serine has been replaced by
a threonine, a very conservative exchange. This small change in
structure, however, produces an adhesive that is two to three times
stronger than the East Coast adhesive (Waite, 1986). This observation
lends support to the view that mussel adhesive might be used as a
model to systematically investigate the relationship between molecular
structure and adhesive function, which could lead ultimately to a
generic glue that can be modified at the molecular workbench for any
number of different moist environments. If broad application is to be

realized for such adhesives, however, functional durability over a wider range of temperatures must be achieved.

Soft-Tissue—Based Materials

Nature has developed exceptional designs for "ultrasoft" materials and for interfacing soft and hard materials with capabilities well beyond present day technology. Exposing the physical and chemical principles that underlie the special features of these materials is certain to stimulate new approaches to design of synthetic materials, parts, and systems. Therefore, the challenges are to extract design lessons from nature especially for development of material technologies that are inaccessible at present. These challenges include preparation of "self-healing" capsular materials that possess tunable and "motile" properties; methods for assembly of soft organic and hard material interfaces that are mechanically, chemically, and electrically compatible; and development of membrane composites that are based on fluid-surfactant interfaces that are supported by tethered polymer networks that possess permeability restriction and mechanical strength.

An example of the potential impact of soft-tissue understanding is the reduction in energy needed to move a body through water when its drag is reduced. Also, in order to prevent detection, there is interest in reducing the hydrodynamic noise a body makes moving through water. Turbulence caused by a moving hull raises drag and hydrodynamic noise. There is no theory at present that links the viscoelastic properties of the surface of a body to its drag or its ability to reduce the amount of hull surface that causes turbulence. Dolphins have a peculiar skin overlying blubber and a collagenous subdermal sheath, and each of these tissue layers has different elastic and damping properties. More importantly, dolphins swim faster and farther using less metabolic energy than calculations would lead one to expect, and it is not clear how they do it. Further studies of the control of damping properties by the micro-, ultra-, and molecular structure of skin, blubber, and peripheral connective tissues of dolphins and of the boundary-layer conditions over their swimming

bodies could lead to new methods for reducing turbulence, drag, and noise.

A second soft tissue is muscle, a soft tissue that has no clear synthetic analogue. It is a transducer, converting electrical signals and chemical energy into mechanical motion. The characteristics of interest are response time, power density in terms of force developed per gram of muscle, and efficiency of power conversion. Piezoelectric transducers can do a similar job but give quite small motions for large applied voltages. Generally, engineers and designers must resort to small electric motors when building, for example, the arms for robots.

Water-swollen cross-linked polymer gels can respond to electric fields by contracting in a way that is superficially similar to muscle. The field drives out a mobile counter-ion. The resulting neutralization of acid groups in the gel causes contraction. Devices have been made with these gels, but the response is slow (1–10 seconds compared with 10–100 milliseconds for muscle), and the power density is low. A soft, light, powerful actuator would have many applications in mechanical engineering ranging from actuators to engines. Intriguing progress toward these objectives has been reported (Urry et al., 1992).

Control of Size and Shape (Assembly, Self-Assembly)

Inherent in the behavior of natural proteins is their assembly into structures of a given size and shape to allow the performance of a specific end-use function. This formation of parts and systems is driven by local geometry and molecular forces and does not require additional "shaping and machining" steps. The ability to design synthetic systems capable of assembling in an analogous fashion would have obvious practical impact.

For the purpose of this report, the determination of shape in biological systems needs to be considered at the level of hierarchical matrix formation. This is between the level of the component macromolecules, whose shapes determine their possible hierarchical interactions, and the level of whole cells, which appear almost

shapeless after isolation from their attachments to other cells and to adjacent extracellular matrix.

Although the shape of an industrially produced article is defined by a set of dimensions that is measured with an externally applied scale, biological shape is determined by the history of internal manufacture of the object, as described in Chapter 2. A hallmark of biological matrix formation is the interaction beween matrix and the cell that adheres to it while manufacturing more of the same material. Previously it was mentioned that cells can be bioengineered to produce and secrete specific macromolecules. Up to now such cells, usually bacteria, yeasts, or insect cells, have been grown in suspension culture, without any specific orientation. For example, the previously mentioned bacteria that secrete cellulose are grown in suspension culture, which produces a random tangle of cellulose fibrils. However, if such cells were provided with cell surface receptors that attach to cellulose, then they could initially orient by attaching to previously made cellulose fibers. Their matrix production would thereby become vectorial with respect to the substrate to which they attach. The initial substrate that is provided to the cells could be structured by weaving, knitting, etc., and the subsequent matrix would be built on to that. The activities of the attached cells could be modulated in various ways, for example, to suppress or enhance cell replication locally and thereby produce patterns of increased concentrations of manufacturing cells. Cells have been engineered to express new receptors at their surfaces by inserting suitable genetic information into them. Furthermore, composite materials could be produced by replacing the initial manufacturing cells later by another set that have been engineered to produce a different matrix macromolecule.

It was previously noted that biological shape emerges partly due to local sculpting. Highly controlled enzymes, such as some collagenases, and their inhibitors, are secreted by cells for limited, local and short-lived action. These enzymes may only modify their substrate, rather than totally destroy it. Limited etching, removal of material, is well established in the manufacture of microelectronic

devices and might have its counterpart in the above scheme of vectorial matrix production.

Some natural self-assembling systems have a defined size, such as some vesicles, while other self-assembling systems are indefinite in extent, such as unstrained crystals. Proper function requires that system size be controlled as well as system shape.

Some examples of methods to control and limit growth are

- controlling the amount of material available for the transformation (the control mechanism is a time-dependent chemical potential);
- controlling the molecular geometry of vesicles;
- termination, due to build up of strain, of synthesis reactions within the molecule being created; and
- diffusion limited aggregation.

The successful translation of these principles to synthetic materials could lead to the integration of the materials synthesis and processing steps of part fabrication.

TECHNOLOGICAL OPPORTUNITIES

Biomedical Materials

There is a recognized societal and economic need for synthetic hierarchical materials with appropriate mechanical and functional performance characteristic properties for use in biomedical applications. This need represents a motivating opportunity for the scientific community to develop these materials.

A brief summary of articular cartilage and diarthrodial joints has been presented (see Chapter 2) as a paradigm for hierarchical materials and structures with nanoscale, ultrascale, microscale, tissue-scale, and macroscale features that enable the performance critical to function. Nanoscale structures such as the charged groups

on the proteoglycan molecules provide the electrochemical bases for Donnan osmotic pressure and charge-to-charge repulsion. Ultrascale structures of proteoglycan aggregates and the collagen network provide the organization for the microporous solid matrix and its essential material properties. Microscale structures include specific cell types (chondrocytes), pericellular, territorial, and interterritorial extracellular matrix organization. These cells manufacture and organize the molecular building blocks and maintain the collagen-proteglycan extracellular solid matrix around themselves by a slow but balanced metabolic process. At the tissue-scale, articular cartilage possesses a set of unique nonlinear, anisotropic and nonhomogeneous material properties that seem to have been specifically designed to provide excellent long-term tribiological (friction, lubrication, and wear) functions at extremely high loads. Finally, at the macroscale, articular cartilage is the bearing material that provides the smooth, near frictionless function required of diarthrodial joints.

The challenges in developing a manufacturing process to produce synthetic hierarchical materials with these required mechanical properties and functional characteristics are great. First, articular cartilage and other biologic tissues have very complex compositional make-ups and ultrastructural organizations. Second, the tissue is manufactured by tissue-specific cells in-situ. These cells are regulated by as yet unknown control processes, which control the production and assembly of the biomacromolecules and organize these macromolecules into an exquisite fabric that is the tissue. It is unlikely that any synthetic process can be developed in the near future that will duplicate the ability of the specific cells to manufacture and organize a hierarchical material with such fine ultrastructural features. However, a hybrid approach has been taken by some researchers, where synthetic grafts have been produced that are made of biocompatible resorbable matrices such as polylactic acid or copolymers of lactic and glycolic acids. These grafts serve as scaffolds for the specifically seeded cells (Cima et al., 1991). These synthetic matrices are not subject to immune reactions. Other gels made of collagen and glycosaminoglycan seeded with cells also show promise

as graft materials for skin and blood vessels. However, for most gels currently available (e.g., fibrin clot that is used for joint surface repair), the material properties are probably insufficient for use in diarthrodial joints where the applied stresses are very high. Development of strong, cohesive, porous, permeable, resorbable gels that are capable of sustaining high stresses and strains and of providing a supporting and protecting environment for the seeded cells is a major challenge for future biomedical researchers interested in developing synthetic hierarchical materials for clinical use.

Improved Membranes and Membrane-based Devices

Improved membrane selectivity is desirable in the areas of water purification, protective clothing for those handling hazardous materials, outdoor clothing and shelters, gas separations, industrial purification processes, etc. Coupled with this is a need for improved stability and increased lifetime for these membranes and mechanisms, in order to reduce fouling. One approach to solving these problems is to incorporate responsive channels and self-repair ("living membranes") or self-cleaning attributes that are patterned after natural membrane systems. For a better understanding of membrane structures in terms of processing and assembly, the incorporation of responsive channels is key. Additional questions lie in the realm of suitable substitutes for water as plasticizers in these materials and in approaches to biomimetic membrane design.

Smart Materials

Natural systems have the ability to sense their surroundings and to respond to impulses or changes in conditions by changing properties or initiating self-preservation or repair responses. The development of smart materials, which integrate the functions of sensing, actuation, and control, can benefit greatly from lessons gleaned from the studies of these biological systems (Rogers, 1992). Passively smart materials

respond to external change without assistance, often through phase changes or transitions in fundamental properties. Actively smart materials utilize feedback loops to recognize changes and initiate appropriate responses (Newnham and Ruschau, 1990; Newnham, 1993).

Opportunities for application of smart materials systems in structural applications generally focus on reduced component mass and adaptive functionality aimed at improving structural efficiency, durability, and safety. Examples of smart materials applications include load and vibration alleviation systems, failure sensing and repair, and shape memory. Challenges in sensor development and integration of sensing and response functions with practical structures need to be addressed to realize the potential of smart materials (NRC, 1994).

For example, important lessons can be learned by studying how sea urchins control the material properties of their bodies as a function of the local environment. Sea stars, sea urchins, and sea cucumbers (in fact, all echinoderms) can control the viscosity of their body wall and other connective tissues. Such tissues can be stiff enough to act as ligaments at one moment and undergo 30 percent extension the next. The change in stiffness and extension is reversible but not elastic, and an animal can cycle through these different states of stiffness-and-compliance, stretching-and-recovery dozens of times a day throughout its multiyear life without the materials showing wear or fatigue. The viscosity of the tissue is modulated by divalent cations, chiefly calcium, which form labile links in a mixture of collagen and glycoprotein molecules. A ganglion of nerve cell bodies whose long fingerlike processes (axons) carry chemicals to all parts of the ligament sits on each ligament. Thus, an important aspect of "smart materials" is sensing. In the case of echinoderms, these biological sensors (receptors) detect neurotransmitters from the nerve cells and in response allow a local increase in the concentration of divalent cations.

An interesting class of nonbiological sensors is that of membranes or thin films adsorbed onto a surface. The chemical sensor consists of arrays of these films or membranes, each sensitive to different materials. There is every expectation that these sensors can

be made with architectures similar to those of presently available microchips, with competitive cost/performance characteristics.

Functionally Gradient Materials

Functionally gradient materials (FGM) are defined as materials in which a continuous spatial change in composition or microstructure gives rise to position-dependent physical and mechanical properties that can extend over microscopic or macroscopic distances (Ramesh and Markworth, 1993). Natural materials with functional gradients abound. Examples of materials with functional gradients that are discussed in this report include articular cartilage and bone. FGM can result in changes or orientation of constituents. For example, articular cartilage exhibits gradients in collagen/proteoglycan concentrations and in collagen fiber orientation. Often, as with cartilage, FGMs are used to provide an interfacial transition between dissimilar materials or to provide multiple functions.

Synthetic FGMs can be produced from mixtures of metals, polymers or ceramics in virtually any combination. A large part of the research in FGMs has focused on coatings and transitions for high-temperature aerospace applications like hypersonic aircraft and advanced turbine engines (Perepezko, 1991; Ramesh and Markworth, 1993). Generally these systems transition from high-temperature resistant ceramics to metallic structural alloys. FGMs have been produced using vapor-phase synthesis, powder techniques, thermal spray processes, and self-propagating high-temperature synthesis.

Another interesting area of research is surface gradients, where the nature of the surface is varied continuously with position (Elwing and Golander, 1991). Gradients in surface areas have been produced that cause water to move uphill (Chaudhury and Whitesides, 1992). Surface gradient techniques may find applications in processing, which will allow selective deposition or coating processes, or in tailored membrane or sensor applications.

The development of functionally gradient materials is still in its early stages. The biggest challenge is in scaling the processes to

practical size components while maintaining the precise control and consistency needed. The study of gradients in natural materials may provide direction for architectural design, fabrication processes, and potential applications for FGMs.

Design and Assembly of Complex Composite Parts

Competitive composite parts require three structural elements to be controlled in a manner that leads to a finished part that possesses the desired mechanical, thermal, and environmental properties in three dimensions. These elements are matrix uniformity, fiber orientation, and fiber-matrix surface interaction. Current methodologies are highly labor intensive, are not amenable to complex shape formation, and present significant problems in performance assessment. Often, machining, polishing, etc., is necessary to achieve the finished part shape and surface characteristics required for the application. In contrast, biological systems often contain complex and sophisticated fiber-reinforced composite "parts" examples range from trees to bones), which exhibit superb performance over extended lifetimes, are capable of healing, and are produced directly as finished parts from cell-based manufacturing plants. It is instructive to compare the "steps" of synthetic and biological fabrication technologies.

SYNTHETIC	BIOLOGICAL
Produce Reinforcing Fiber	Produce Matrix "Scaffold" for Part
Treat Fiber Surface	Form Crystal Directing Surface
Impregnate Fiber with Matrix	Fill with "Gel"
Line Up Prepeg Plies in Mold	Replace Gel with Oriented "Fiber"
Cure/Shape Part	

In both cases, the materials employed and the final composite structure will contain key hierarchical structural elements. In the natural system, however, the hierarchy is a key to performance. Understanding and, where appropriate, mimicking the structure and manufacturing logic of natural hierarchies offer an opportunity to leapfrog current composite technologies and realize the promise of synthetic composites, which has proven elusive to the materials community for more than two decades.

The toughest materials are known to raise the energy required for tearing by diverting cracks away from their preferred directions of propagation. A horse's hoof is difficult to split vertically (in the direction up the horse's leg). Hoof material contains keratin (the major protein in hair, finger nails, feathers, and rhino horn) in an ordered three-dimensional array such that a crack initiated by a vertical cut will turn and split the material at right angles to the vertical direction (circumferentially in the hoof). As a result, if a split does occur, it will cause the loss of a thin strip of the hoof's three-dimensional fiber array. The relationships between the array and the resistance to impact and control of crack propagation could illustrate new mechanisms of fracture toughness to be used in designing new synthetic materials. In addition, study of the mechanisms of synthesis of hoof material in the horse can be expected to provide hints for the industrial fabrication of such complex three-dimensional fibrous materials. However, improvements over current analysis methods are needed to take full advantage of these toughening mechanisms.

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Appendix A: GLOSSARY OF TERMS

Actin: a protein characteristic of muscle but also found in other types of cells. Actin may exist in a monomeric, globular form that polymerizes to form filaments.

Ampullate gland: the silk-producing gland of spiders.

Aragonite: a form of the mineral $CaCO_3$ with an orthorhombic crystal structure.

Articular cartilage: the tissue that covers bones within freely moving joints (hip, knee, shoulder, etc.).

Axon: a long, thin process of a nerve cell that extends away from the cell body (which contains the nucleus and most of the other organelles) and terminates in numerous small branches.

Cancellous bone: the bone of sponge-like loading within the hard cortical bones.

Carpus bone: a bone of the wrist or part of an animal fore-limb.

Catch connective tissue: the ligaments that attach the calcite spines of sea urchins to muscle.

Cellulose: a fibrous substance that makes up plant cell walls.

Chitin: a structural polysaccharide found in the shell of crustaceans and insects and in the cell walls of fungi. Chitin is a linear polymer of N-acetylglucosamine.

Collagen: a family of filamentous proteins that are organized in a triple helix conformation and that provide tensile stiffness and strength to biological entities.

Cytoskeleton: a submicroscopic intracellular complex of protein, which is believed to account for the mechanical properties of cytoplasm. Actin and tubulin are examples of cytoskeletal proteins.

Diarthrodial joint: a freely moving joint of the body (hip, knee, shoulder, etc.).

Donnan osmotic pressure: the osmotic pressure in a solution of electrolytes that are freely permeable across a semipermeable membrane but are distributed unequally because of the pressure of a nondiffusible charged substance on one side of the membrane.

Epitaxy: oriented growth of one crystalline substance on a different crystalline substrate.

Fibril: an elemental unit of a collagen composed of a number of triple helical collagen molecules; a microscopic fiber.

Ganglion: an aggregation of nerve cell bodies.

Hyaluronic acid: a copolymer composed of glucuronic acid and M-acetylglucosamine and glucuronic units with a molecular weight in excess of 10^5.

Haversian bone: the concentric arrangement of bone cells and inorganic material around a central, blood vessel–carrying canal. Canaculi connect with the central canal, with each other, and with bone cell–containing spaces.

Hemicellulose: a polysaccharide similar to cellulose in that it is insoluble in water and hydrolyzable in acid. Hemicelluloses are probably of smaller molecular dimensions than celluloses and contain, in addition to glucose, xylose, galactose, uronic acid, and other sugars.

Hydroxyapatite: a calcium phosphate that crystallizes into hexagonal platelets and that can be approximated by the formula $3Ca_3(PA_4)_2 \cdot Ca(OH)_2$.

Integrin protein: a protein component of a lipid bilayer membrane that is so intimately associated with the membrane that it can only be removed by using detergents.

Lignin: an organic polymer component in wood.

Living polymer: a mixture of polymer molecules that contain active sites at which polymerization can continue when monomer is added to the mixture.

Lumen: the internal cavity of a hollow organ or organelle.

Mesoglea: the collagenous connective tissue in the body walls of sea anemones.

Metathesis: a reaction in which chemical groups attached to carbon-carbon double bonds are exchanged.

Microfibril: the substructure of a collagen fibril that is composed of associated tropocollagen units.

Nacre: iridescent inner layer of various mollusk shells that consists chiefly of calcium carbonate deposited in thin overlapping sheets with some organic matter.

Organelle: a specialized part of a cell, which performs functions analogous to those of the organs of many-celled animals.

Proteoglycan: a "core" protein linked to many glycosaminoglycan chains, which composes a macromolecule exceeding 10^6 daltons.

Proteoglycan aggregates: proteoglycans linked to hyaluronate chains via a like protein. The molecular weight of this molecule often exceeds 10^7. Its high density of charge groups (carboxyl and sulfate) enable it to provide valuable function in biological tissues.

Appendix B: BIOGRAPHICAL SKETCHES OF COMMITTEE MEMBERS

DAVID A. TIRRELL, *Chair*, received a B.S. in chemistry from the Massachusetts Institute of Technology and an M.S. and a Ph.D. in polymer science and engineering from the University of Massachusetts at Amherst. He was an associate professor of chemistry at Carnegie Mellon University before joining the faculty of the University of Massachusetts at Amherst. His research interests include synthetic and natural macromolecular chemistry, biological materials, and structures.

ILHAN A. AKSAY received a B.Sc. from the University of Washington and an M.Sc. and a Ph.D. in materials science engineering from the University of California, Berkeley. After employment with Xerox, the Middle East Technical University, University of California Los Angeles, and the University of Washington, he joined the faculty of Princeton University in 1992. His research interests include processing science of ceramics, thermodynamics and phase equilibra, and interfacial reactions and capillary phenomena, and bioinspired processing of materials.

ERIC BAER received an M.A. and a Ph.D. in chemical engineering from Johns Hopkins University. After working at E. I. du Pont de Nemours and Company and at the University of Illinois, he

joined the faculty of Case Western Reserve University. His research interests include elucidation of hierarchical structures in natural and synthetic material systems, structure–property relationships, transitional phenomena, and failure and fracture processes.

PAUL D. CALVERT received a B.A. and an M.A. from the University of Cambridge and a Ph.D. in materials engineering from the Massachusetts Institute of Technology. He worked at the University of Sussex and is now a professor at the University of Arizona. His research interests include biomimetic composite materials, polymers, and ceramic processing.

JOSEPH CAPPELLO received a B.S. from the University of California, Davis, and a Ph.D. in biological chemistry from the University of Cincinnati. After working at Syntro Corporation, he cofounded Protein Polymers Technologies, Inc. His research interests include the design and biological production of synthetically designed proteins, assembly and structure of fiber-forming proteins, material properties of fibers and films, and the effect of chain structure and folding on materials processing.

EDMUND A. DIMARZIO received a B.S. from St. Joseph's College, an M.S. from the University of Pennsylvania, and a Ph.D. in physics from Catholic University. He worked at American Viscose Company and Bell Telephone Laboratories before joining the National Institute of Standards and Technology. His research interests include helix-coil transitions in biological macromolecules, liquid-crystal phase transitions, surface polymers, and the kinetics of crystallization. Dr. Dimarzio is interested in phase transitions in polymers as models for self-assembly.

EVAN A. EVANS received a B.S. and an M.S. from Rensselaer Polytechnic Institute and a Ph.D. in engineering science from the University of California, San Diego. After working at McMaster University and Duke University, he joined the faculty of the University of British Columbia. His research interests include mechanics and thermodynamics of biological cell structure motility, interactions between biological membranes, and the physical chemistry and mechanics of synthetic interfaces.

JOHN H. FESSLER received a B.A., a B.Sc., an M.A., and a Ph.D. in chemistry, animal physiology, and physical biochemistry from Oxford University. After working at the Massachusetts General Hospital and Harvard Medical School; the Medical Research Council, England; and the California Institute of Technology, he joined the faculty of the University of California, Los Angeles. His research interests include the biosynthesis of connective tissue and molecular developmental biology.

JOHN D. HOFFMAN received a B.S. from Franklin and Marshall College and an M.S. and a Ph.D. in physical chemistry from Princeton University. After working at General Electric Company, the National Bureau of Standards, the Univerity of Maryland, and Michigan Molecular Institute, he joined the faculty of Johns Hopkins University. Dr. Hoffman is a member of the National Academy of Engineering. His research interests include dielectric phenomena and polymer physics.

MICHAEL JAFFE received a B.A. from Cornell University and a Ph.D. in chemistry from Rensselaer Polytechnic Institute. He is presently a research fellow at the Hoechst Celanese Research Division. His research interests include the structure–property relationships of morphology of crystalline high polymers, phase transition behavior of polymers, and materials.

GEORGE MAYER received a B.S. from Boston University, an M.Met.E. from the University of Oklahoma, and a Ph.D. in metallurgy from the Massachusetts Institute of Technology (MIT). He has worked at the Chrysler Corporation, Ilikon Corporation, MIT, Monsanto Company, the Army Research Office, and the Institute for Defense Analyses. He is presently employed by the University of Pittsburgh. Dr. Mayer's research interests include mechanical behavior of materials, composite materials, corrosion, nondestructive testing, and materials processing.

VAN C. MOW received a B.A.E. and a Ph.D. in mechanics from Rensselaer Polytechnic Institute (RPI). He has worked at RPI, New York University, and the Bell Telephone Laboratories. Presently he is Professor of Mechanical Engineering and Orthopedic Bioengineering at Columbia University. Dr. Mow is a member of the National Academy of Engineering. His research interests include continuum mechanics, classical elasticity and thermoelasticity theory, fluid mechanics, applied mathematics, and biomechanics of synovial joints.

STEPHEN A. WAINWRIGHT received a B.S. from Duke University, a B.A. from the University of Cambridge, and a Ph.D. in zoology from the University of California, Berkeley. He is presently a professor of zoology at Duke University. His research interests include the structure of locomotor and postural systems of animals and plants from the macromolecular through the organism levels of organization.

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13. ABSTRACT (Maximum 200 words)

Hierarchical structures are assemblages of molecular units or their aggregates that are embedded or intertwined with other phases, which in turn are similarly organized at increasing size levels. The multilevel architectures are capable of conferring unique properties to the structure. Hierarchical structures are found in practically all complex systems, particularly naturally occurring ones. Synthetic hierarchical structures can be prepared from metals, ceramics, or polymers, or from hybrids of various classes of these materials.

The Committee on Synthetic Hierarchical Structures made an assessment of the opportunities to prepare hierarchical structures that possess useful and unusual physical properties for civilian and military applications. It conducted case-studies by selecting natural material systems to be used as models for synthetic efforts. It reviewed the state of the art of synthetic techniques and processes for assembling synthetic hierarchical structures. The committee also characterized properties, unusual characteristics, and potential end-use applications for these synthetic systems. Finally, the committee recommended research directions to expedite the understanding of the complex phenomena involved, lead to increased coordination among disciplines, and provide direction for future activities in the field.

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