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13. ABSTRACT *(Maximum 200 words)*
A workshop on the role of hierarchy in the structural properties of materials was held at St. Christopher's Camp 'n Conference Center located in Charleston, South Carolina from May 31 through June 2, 1995. The Workshop participants focussed on three related topics: (i) The lessons to be learned from hierarchical structures in biological composites; (ii) The application of theoretical modeling to structure-property relations in hierarchically structured materials; and (iii) Synthesis and processing strategies for the fabrication of new synthetic materials. A goal of the workshop was to establish better communication among the many different disciplines working in the area of materials property research, especially those directly involved with biomimetic or biogenic systems. A previous NRC report highlighted the importance of this class of materials and recommended that "the academic and industrial sectors of the materials community prepare for [the development of hierarchical materials] through implementation of appropriate educational and engineering programs...". Technological and scientific opportunities identified in this report need to be pursued through collaborative research efforts between academia and the industry. While most of the discussions focused on lessons from biology, it was generally agreed that a more fundamental definition of structure-property optimization through structural hierarchy needs to be developed and that economically attractive synthesis and processing methods are needed to reduce these concepts to practice.

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Final Report on

STRUCTURAL HIERARCHY IN MATERIALS: PROCESSING AND PROPERTY OPTIMIZATION

Workshop
May 31 – June 2, 1995
Camp Christopher, South Carolina

submitted to

U.S. Army Research Office
Materials Science Division
4300 South Miami Boulevard, PO Box 12211
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Workshop on

Structural Hierarchy in Materials: Processing and Property Optimization

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Workshop on

Structural Hierarchy in Materials: Processing and Property Optimization

Introduction

A workshop on the optimization of materials properties through rational design of structural hierarchy was held at St. Christopher's Camp 'n Conference Center located in Charleston, South Carolina from May 31 through June 2, 1995. The workshop focussed on three related topics: (i) Lessons to be learned from hierarchical structures in biological composites; (ii) Theoretical modeling of structure-property relations in hierarchically structured materials; and (iii) Synthesis and processing strategies for the fabrication of new synthetic materials.

The organizers set enhanced communications and connections among the many researchers working within distinct disciplines yet sharing an interest in the concept of hierarchy as a primary goal for the workshop. They were encouraged in this by comments in then-recent NRC report[1] that stressed the importance for defining the role of hierarchy in material properties and the expected benefits that will ensue from understanding structural hierarchy. The NRC report noted that "the academic and industrial sectors of the materials community [must] prepare for [the development of hierarchical materials] through implementation of appropriate educational and engineering programs..."[1] The technological and scientific opportunities identified in the NRC report need to be pursued through collaborative research efforts formed between academia and industry. Accordingly, participants were invited from the academic, government, and private sectors, to combine intellectual rigor with the realities of end-user needs. In this the workshop departed from previous research in hierarchical systems which emphasized what could be learned from the study of biological structures.[2,3,4]

Workshop Goals and Structure

The participants sought to establish a common foundation for continuing research in structural hierarchy, seeking a more fundamental definition of the structure-property relationship and the optimization of structures through the development of appropriate hierarchies. Such information is needed if new technologies are to be achieved. Subsequent advances will need to build upon the new understanding, demonstrating the utility of the new knowledge through the development of economically viable syntheses and processes and the fabrication of superior material systems.

Accordingly, the workshop was organized around three topical areas: (1) *Lessons from Biology on the Nature of Hierarchically Structured Materials*; (2) *Current and Expected Future Developments in Theoretical Models Examining Structure-Property Optimization through Hierarchical Structuring*; and (3) *Potential Developments in Synthesis and Processing for the Successful Fabrication of Hierarchically Structured Materials*. The first part of the workshop, covering biogenic materials, provided the frame that defined the general interest of the entire workshop: to review (i) what is known about and (ii) what can be learned from the study of naturally-occurring hierarchical systems. The definition of appropriate goals for the second and third parts of the workshop, due to limited experience with synthetic hierarchical materials, was informed by the studies on biogenic composites. Thus, two key observations were taken from previous studies of biogenic composites and used to further define the goals for the second and third parts of the workshop. In essence, these two essential lessons were defined as:

(a) First, composite structures are themselves the building blocks for larger scale composite structures.[3-4] Nested levels of structural hierarchy appear to yield improved properties for particular functions, but connections between hierarchical design and property optimization are based solely on empirical observations. Thus, future research must develop appropriate statistical mechanical models linking properties and hierarchical structure.

(b) Secondly, whereas the principle of hierarchical design has already been applied to synthetic composites, the smallest length scale of synthetic hierarchy still lies within the micrometer (10^{-6} m) range.[5] Since many material properties (e.g., crack propagation) do not scale linearly with size,[6] hierarchy at the nanometer scale results in materials properties which differ significantly from predictions based on simplistic "rule of mixing" models. To better define the bulk properties of the constituents it becomes necessary to extend concepts of hierarchical design down to the nanometer range to produce materials with improved properties. Thus, novel synthesis and processing methods are needed to build materials with nanometer-scale features.

In the second area of the workshop regarding structure-property optimization, the key issues raised consisted of the following set of queries:

(a) Is structural hierarchy characteristic in some materials indicative of an optimization process?[7,8]

(b) How robust is hierarchy when a number of different properties or effects are relevant to the optimization process? For example, does the competition between mechanical processes and transport processes (where the interface plays a major role) destroy hierarchy?

(c) Do hierarchical laminate structures optimize the *nonlinear* elastic response of a composite?

(d) Can evolutionary processes leading to apparently optimal hierarchical structures be explained theoretically?

(e) Can a framework be constructed to quantitatively characterize the structure of hierarchical composites in which the number of levels is neither infinite nor self-similar (i.e., fractal)?[9-12]

The key questions within the third part of the workshop, devoted to potential developments, focused on pattern formation at the submicron length scale, the most difficult challenge faced in the fabrication of synthetic materials. In biological systems, organic molecules self-assemble into complex structures organized at the mesoscale, a scale of tens of nanometers. Organization at these length scales is difficult for the small unit cell inorganic materials typically used to impart hardness. Structurally organized organic surfaces catalytically or epitaxially induce growth of specifically oriented, dissimilar constituents. In this way, soft organic structures tens of nanometers in size act as templates to macroscopically orient and shape harder and simpler inorganic crystals. One of the workshop goals in the third topic area was to combine respective experiences and knowledge to better understand the assembly and templating processes, thereby helping to set guidelines for the practical design of nanocomposites with desired shapes and orientations. Another goal was to better understand how the surface of a material influences the formation of a very dissimilar material. Taken together, the intent is to develop design and process parameters for organic/inorganic composites through the control of the structural organization from the centimeter length scale (required for usable materials) to the Ångström scale that controls the interfaces. Ultimately, the crucial steps will be determining new techniques to control mesoscopic organization and to translate those into methods for building hierarchical structures with improved performance.

Discussions

One purpose of the workshop was to prepare a brief report on important materials problems and the development opportunities in the areas the processing and property optimization of hierarchical materials systems. Different approaches were emphasized: (i) defining the desired performance characteristics of the materials system, (ii) listing possible avenues for achieving interactive performance characteristics, (iii) identifying and ranking in importance the technology barriers for each approach, and (iv) assessing the probability of technology success (in both short and long terms) and the expected impact of success for each approach. Three 'teams' of participants were formed into discussion groups that met after the general presentations. Each team was asked to used a list of topical questions as a guide to their respective discussions:

1. What are the desired performance characteristics required for the applications of the materials systems?
2. What approaches would be suitable for achieving the interactive performance characteristics?
3. What are the bottlenecks to realizing such applications, in terms of both basic research and technological development?
4. What are the short- (next 5 years) and long-term (next 20 years) opportunities in the areas of your expertise?
5. What scale of research investment is required?
6. If successful, how widespread an impact will the technology have?

Performance

In general, an appropriate definition of performance depends upon the application or applications envisioned. In truly bioinspired systems, the concept of *multifunctionality* is extremely important. A structure may not merely meet the requirements for its perceived use but may also provide redundancy to other systems within the biological entity. Beyond specific functionality however, a short list of generally desirable performance characteristics includes: the self-repair of flaws, malfunctions, or damages; modes of graceful failure that protect overall system integrity; environmental robustness; and long life cycles, especially in situations involving cyclic events ("on/off", cyclic fatigue, and so forth).

Materials that meet these requirements can then be more properly seen as systems, integrating structures at different length scales and composed of a variety of substances of differing properties (akin to graded materials), with the possible addition of stimulus/response mechanisms to allow the material to adapt to circumstances. Under this interpretation of materials, a materials system very similar to biological systems has been defined. The need for hierarchy arises from the ability to tailor properties across many length scales, permitting geometric averaging across the entire system. That is, the system can spread damage or stress across a wider area or throughout a greater volume, rather than suffering a localized event, and thereby enhance reliability of the whole system while ameliorating the extent of damage in any one portion of the material.

The question can be raised concerning the need for biomimetic lessons in the design of a specific device, such as a vehicle. It is not necessarily appropriate to look to biology to seek answers for the proper construction of an integrated, large-scale device. Rather, it may be more appropriate to reduce the large system into its components and determine the operational requirements for each. Then biological structures can be examined to see how natural structures evolved to meet similar requirements. However, it is likely that synergistic relationships will often be found between biological systems, and these relationships will inform the design-making process in the fabrication of synthetic analogs.

Approaches

Approaches to satisfying the performance requirements made of new hierarchical materials will depend primarily upon adopting a "systems approach," a holistic treatment of the material as an integrated unit rather than treating it as a unit or as a collection of component parts. As in the example of a vehicle, while it may be appropriate to reduce a system to components to better define each one's operational characteristics, the effect of combining these components into a single operating unit cannot be ignored. Biological systems exhibit multiple levels of redundancy and a range of response mechanisms, often related to the interactions between the components that comprise the biological structure. The evolution and performance of structures within a living system can be determined by the presence of the other structures within the system. Likewise, new material systems must also account for possible interactions between the components within the system, with particular attention paid to interactions which serve to either enhance or degrade the performance of one or more of the other components and thereby affect the overall performance of the device of interest.

Obviously, this will require some restructuring of the way in which materials problems are addressed. First and foremost, the very nature of hierarchy in materials must be elucidated. There must be closer interactions among researchers across the spectrum of disciplines, from basic engineering through fundamental science, coupling laboratory models with theory and practical applications. The overarching question will be one of *utility*: does the proposed system satisfy the requirements of the proposed application? Biological systems can and should provide a base upon which broader definitions of hierarchy can rest, but synthetic systems cannot be limited by biological analogs. Instead, researchers will need to work out of their familiar modes to take advantage of the new opportunities offered by the eventual understanding of hierarchy.

Bottlenecks

There are many areas of ignorance and uncertainties within the study of materials, which provide impediments but also provide opportunities for new studies on and interest in the realization of hierarchical materials. A major bottleneck is the virtual absence of biologists from discussions concerning the engineering aspects of biological systems. Although there is a burgeoning interest among biologists in the use of systems analysis with respect to the evolution of living structures, there appears to be little cross-over between these scientists and the broader community of scientists and engineers, too many of whom remain ignorant of advances in the biological sciences or lack the requisite familiarity with the language of biology.

The broader question of what can be learned from nature becomes the focus. What can be learned, or still needs to be learned, from studies on multifunctional components, benign processing (e.g., low temperature and pressure, aqueous-based processes), and economy in processing? Biological structures grow using available materials, often dispersed or present in low concentrations, can accumulate and store essential substances, and have some ability to work around transient shortages. But there are at least two serious constraints on biogenic processes: growth is slow and systems evolve in response to survivability, irregardless of efficiency. As a result of these considerations, biological systems are not always suitable guides to the synthesis of new materials. A screening process is needed, one that distinguishes the potentially useful from the merely interesting. In this, communication between biologists and other researchers becomes more important—the biological community should be instrumental in determining what processes offer the highest return on investment with respect to eventual process development.

Beyond the issue of connections between the biological sciences and other disciplines, several outstanding areas of investigation suggest themselves:

- Delineating the importance of hierarchy by determining the smallest length scale at which hierarchical structures influence the overall material properties and the number of levels needed to optimize structures for specific properties.
- Optimizing structures for non-linear properties (such as failure), and incorporating interactions among the different length scales that define the material of interest. Delineating size effects and incorporating structural variables within any model of non-linear behaviors.
- Phase diagrams for "parallel processes," which are usually history-dependent. These couple with the need for more information on natural processes, such as the synthesis of seashell, which rely on the interaction of multiple functionality within the overall system.
- Modeling non-equilibrium systems, recognizing that most system models focus on equilibrium states whereas active systems are usually <u>not</u> at equilibrium.
- Coupling models with experimental results, necessary to check the model's veracity and accuracy for predicting behavior. This will require strong connections between the modeling community and the experimentalists, requiring both to tailor their respective interests to a more general understanding of material properties.
- Improved rapid manufacturing techniques for the fabrication of hierarchical materials, beginning at the micro- and/or nanoscale, and focusing on the incorporation of multiple length scales in materials.

Opportunities

Opportunities in the realization of hierarchical structure developments are seen to cover a wide range of potential applications and eventual commercialization. Areas of short-term (<5 years to realization) and longer term (>5 years) were described. Short-term realizations will come in the areas of composite material development, especially with respect to mechanical properties and processing. There are likely to be some notable successes in the areas of nano- and microprocessing techniques, with further refinements in the resolving power of rapid prototyping methods such as stereolithography and laminated object manufacturing. Self- and co-assembly, whether spontaneous or directed, will continue to interest teams of researchers, and new product developments should begin to appear within the five-year time frame. Theoretical models will progress into optimization of non-linear behaviors, emphasizing new model systems while enjoying expanded computer processing power. Perhaps most importantly, more researchers will recognize the opportunities that exist in studies on hierarchical materials and biomimetic processes. The expanding interest in benign processing and the realization that properties can be tailored by fabricating systems across length scales will begin to be seen in the academic community, with some spill-over into industry and government laboratories.

Long term opportunities will include developments in adaptive materials, systems that will respond to the environment. Biogenic methods for fabricating materials will become available, although the rate of fabrication is not likely to be high. Instead, the biogenic models will provide guidance for synthetic processes for the economic production of simple devices. Scale-up will remain an issue, as the translation from the biogenic model to pure synthesis will remain a bottleneck. Advanced modeling techniques will feed into rapid prototyping, paralleling increases in computational power and advances in the resolutions achievable in 3-dimensional lithographies and patterning. The latter will benefit from advances in field-directed fabrication, using fine particles and/or liquid precursors manipulated by the application of electromagnetic fields to the building of the requisite structures. Miniaturization will be readily achieved at the nanometer scale, and microscale devices will be integrated into material systems. Initial product developments will be most likely focussed on biosensor, computational, and communication applications. "Smart materials" will be composed of interconnected structures, comprising multifunctional and/or interchangeable modules constructed via microfabrication processes.

Scale of Investment

The scale of investment is a difficult question to address. The need to cross disciplines requires the cooperation and coordination across departmental boundaries within institutions but also demands the same across institutions. A critical level of funding, sufficient to fund six to eight multi-disciplinary programs would be on the order of $10M/year. A sustainable level is unknown. Regardless of the extent of funding that may be available, a primary factor to the success of this research effort will be the stability of the funding base; episodic or fluctuating funding will not encourage the formation of research centers or multi-disciplinary research teams. To maintain the interest in the goals of hierarchical materials, support must be stable. The responsibility of the research teams is then obvious: to justify the high level of support with significant and far-reaching results.

Impact

The success in applying the concept of hierarchy to materials science will result in a redefinition of materials science. Long a multi-disciplinary program, materials science will expand into the areas of biology and systems engineering. Processing will become a centerpiece of the materials researcher's interests, by setting the limits of performance. Tailored materials and composite structures will more fully integrate the subdisciplines of metallurgy, ceramics, and polymer engineering.

The private sector will benefit from the advent of design tools for multiple length scale fabrication, along with the methodologies for rapidly fabricating prototype and product materials. More efficient use of materials and the optimization of performance through processing will reduce the scale of materials synthesis, its related costs, and the use of high-grade raw materials. More environmentally benign methods of production will reduce both the volume and the toxicity of waste generated by the new processes. New materials will be more reliable, possibly self-repairing to some extent, and more resistant to the environment. Integrating systems design, fabrication, and optimization will change the nature of systems analysis, leading to tailored material systems optimized for specific applications.

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Workshop Schedule

Wednesday, May 31, 1995:

07:30	Registration
08:30 - 09:00	Introduction: W. C. Simmons, E. Baer, and I. A. Aksay

Session I:
Lessons from Biology on Hierarchically Structured Materials
Chair: Wilbur Simmons, US Army Research Office

09:00 - 09:45	Steve Wainwright, Duke University, *"Materials that drive animal locomotion"*
09:45 - 10:30	Eric Baer, Case Western Reserve University, *"Hierarchical structures in soft connective tissues - lessons from biology*
10:45 - 11:30	Mehmet Sarikaya, University of Washington, *"The making of a hierarchically structured biocomposite: shell of mollusks"*

Session II:
Theoretical Models on Structure-Property Optimization through Hierarchical Structuring
Chair: Eric Baer, Case Western Reserve University

11:30 - 12:15	Robert Kohn, Courant Institute, *"Elastically extremal composites and structures"*
12:15 - 13:15	*Lunch* (served in Conference Dining Room)
13:15 - 14:00	Steve Cowin, CCNY, *"Kelvin mode coalescence in bone and wood"*
14:00 - 14:45	Salvatore Torquato, Princeton University *"Structure and properties of hierarchical composites"*
15:00 - 15:45	Roderic Lakes, University of Iowa, *"Structural hierarchy in cellular solids and in high-loss viscoelastic composite materials"*

Session III:
Synthesis and Processing Methods for the Fabrication of Hierarchically Structured Materials
Chair: Ilhan Aksay, Princeton University

15:45 - 16:30	Greg Olson, Northwestern University, *"Systems design of materials"*
16:30 - 17:15	Anne Hiltner, Case Western Reserve University, *"New composite materials by microlayer coextrusion"*

Thursday, June 1, 1995:

08:30 - 09:15	Brian Cox, Rockwell International, *"Lockup, chains, and the delocalization of damage"*
09:15 - 10:00	Jack Lackey, Georgia Tech., *"Biomimetic structures through chemical vapor infiltration"*
10:15 - 11:00	David Kaplan, US Army, Natick RD&E Center, *"Hierarchy and biomineralization - experimental approaches"*
11:00 - 11:45	Ilhan Aksay, Princeton University, *"Processing of hierarchically structured materials through selfassembly"*
11:45 - 12:30	Robert Prud'homme, Princeton University, *"Hierarchical structures through stereolithography"*
13:30 - 14:15	Shi-Oing Wang, Case Western Reserve University, *"Polymer melts as structural materials: scaling relations and melt-solid interfacial interactions in processing"*
14:15 - 15:00	Masanori Hara, Rutgers University, *"Ionic interactions in polymeric materials and hierarchical structures"*
15:00 - 15:45	Lynn Penn, University of Kentucky, *"Toughening impenetrable interfaces by tethered polymer chains"*

Session IV:
Report Preparation

15:45 - 17:30	General Discussion and Subgroup Discussions

Friday, June 2, 1995:

08:30 - 10:00	Subgroup Discussions
10:15 - 11:45	Subgroup Reports
11:45 - 12:00	Discussion, Summary, Closure
13:00:	Workshop Concluded

Abstracts

Materials that Drive Animal Locomotion

Stephen A. Wainwright, Department of Zoology, Duke University, Durham, NC

All animals are mobile polymeric machines that are actuated by a polymer that shortens forcefully (muscle). Reaction to muscular forces is accomplished by a variety of hierarchical polymeric and polycrystalline mineralized materials. Forces are reacted unidirectionally by tendons of fibrous collagen (protein in vertebrates) and chitin (polysaccharide in arthropods). Internal hydrostatic pressures are reacted by 2-dimensional sheets of polymeric fibers in oriented arrays. Ridged materials (bone, scallop shell, lobster shell, feather) forming the levers that power locomotion are hierarchical arrays of oriented polymers and mineral crystals. Insect flight, mammalian running and jumping and swimming of scallops, sharks, and whales depend on elastic energy release of tendons and membranes. Force transmitting junctions between materials are often shear rather than simple tension. Locomotor performance depends on compatibility of materials through hierarchical levels.

Hierarchical Structures in Soft Connective Tissues - Lessons from Biology

Eric Baer, Department of Macromolecular Science, Case Western Reserve University, Cleveland, OH

Hierarchical structures in biocomposite systems such as in collagenous connective tissue have many scales or levels, have highly specific interactions between these levels, and have the architecture to accommodate a complex spectrum of property requirements. As examples, the hierarchical structure - property relationships are described in three soft connective tissues: Tendon, intestine, and invertebral disk. In all instances, we observed numerous levels of organization with highly specific interconnectivity and with unique architectures that are designed to give the required spectrum of properties for each oriented composite system. From these lessons in biology, the laws of complex composite systems for functional macromolecular assemblies are considered.

The Making of a Hierarchically Structured Biocomposite: Shell of Mollusks

Mehmet Sarikaya, Department of Materials Science and Engineering, University of Washington, Seattle, WA

The structure of red abalone, *Haliotis rufescens* (a gastropod), as well as those of Nautilus, *Nautilus pompelius* (a cephalopod) and pearl oyster, *Pinctada margaritifera* (a bivalve), is made up of two sections: inner nacreous (mother-if-pearl) and outer prismatic. Two polymorphic forms of CaCO3 constitute the inorganic component (each 98% of the overall composite) on the inside, i.e., aragonite (orthorhombic) and on the outside, i.e., calcite (rhombohedral). Each section forms in a unique way into significantly different microarchitectural conformations, but with an overall microstructure which is a functionally gradient composite having hard, outside, and tough, inside, layers, whose room temperature mechanical properties far surpass that of "high-technology" covalent ceramics.

Morphology and crystallography of the shell microstructure are not random, but highly ordered and predictable. For example, in the brick-and-mortar microarchitecture of the nacreous section, the aragonite is in the form of platelets (0.25 μm thick, and 5 μm in edge length) that are surrounded by a thin (5-10 nm) organic matrix, which appears to be a molecular-composite of proteins and polysaccharides. Detailed electron microdiffraction reveals that the aragonite platelets form a multiply-tiled space-filling structure with hierarchical twinning. A model, from this result, gives the organization of possible nucleator proteins that order into a long-range near-hexagonal coincidence-site-lattice within the organic matrix which itself may actually be a pseudo-membrane. Based on this model, crystallography and morphology of the platelets, and the growth of the shell into a spiral macroform can be explained. This is a significant lesson toward engineering complex, but highly-ordered, bioduplicated-synthetic materials microstructures.

The central issue in nacre, and in other mineralized tissues, is the question of how organic matrix may control the formation of the inorganic phase and influence its two- and three-dimensional order. Intrinsic in this issue is the nature of proteins, or other macromolecules, which may be major factors for the nucleation and growth of the inorganic phase. Our results gives new insight into how this might take place in nacre. It is desirable, therefore, to isolate the macromolecules, characterize them (including their genetic sequence), and to decipher their effect in crystal formation. The knowledge base regarding biomineralization has reached the point where creation of new protein sequences to organize mineralization can be realistically considered. One unique approach may be to mimick the organismal pathway in nacre formation to organize, by self assembly, the membrane-bound proteins that have affinity to specific inorganic crystal surfaces and that are selected via a combinatorial approach, and to use this protein-membrane complex as a substrate to nucleate and to control a directed growth of inorganic particulates and thin films, including iron oxide and calcium carbonate.

Elastically Extremal Composites and Structures

Robert V. Kohn, Courant Institute, New York University, New York, NY

The macroscopic properties of a composite depend in a subtle way on the geometry of the microstructure. Composites with extremal effective behavior are special interest. There are some classical examples -- for example Hashin's "concentric sphere" microstructure, which produces a composite with extremal bulk modulus. There are also some general techniques for constructing elastically extremal composites -- particularly in the two-component case, through an algorithm based on the Hashin-Shtrikman variational principle and sequential lamination. It should be emphasized, however, that elastically extremal microstructures can be far from unique. The Vigdergauz microstructure provides an enlightening example. It achieves the same effective bulk modulus as the concentric sphere construction (for mixtures of two isotropic materials in plane elasticity), but it is totally different and much more highly ordered.

The optimization of microstructure is just structural optimization on a microscopic length scale. There is an extensive literature on structural optimization, and much numerical work on how to improve or optimize structures. This work has mostly concentrated on macrostructure not microstructure, but the distinction is quite artificial. Recently, extremal composites have been used as a "regularization," and as a tool for "topology optimization." Also, numerical structural optimization has begun to be used at the microstructural length scale, as a tool for identifying new examples of elastically extremal composites.

Kelvin Mode Coalescence in Bone and Wood

Stephen C. Cowin, The City College of The City University of New York, New York, NY

Two natural composites, wood and bone, have special types of orthotropic material symmetry characterized by coalescence of some of their Kelvin modes. Since both of these natural composites are known, *in vivo*, to have mechanisms by which their microstructure optimally adapts in time to the mechanical environmental load they experience, it may prove profitable for man-made composite design to understand the physical microstructure that endows these natural composites with these special types of orthotropic material symmetry. The observed Kelvin mode coalescence in natural composite materials raises the possibility that nature has devised a mechanism for minimizing or mitigating the damaging effects of repeated cyclic loading as the mechanical loading on both living bone and trees is cyclic.

This presentation will focus on softwood. The hierarchical composite structure of softwood will be reviewed and special mechanical properties of softwood will be highlighted.

Structure and Properties of Hierarchical Composites

Salvatore Torquato, Department of Civil Engineering and Operations Research,
Princeton University, Princeton, NJ

The preponderance of studies on composites have focused on those with a single characteristic length scale. Composites with factual structures (i.e., with self-similarity on all length scales) are popular multi-scale models. However, biological materials are hierarchical composites in which the number of levels is neither infinite nor self-similar. I shall briefly review our state of knowledge regarding structure/property relations for single-scale composites. New results for hierarchical composites with finite number of levels will also be presented.

Structural Hierarchy in Cellular Solids and in High-loss Viscoelastic Composite Materials

Roderic Lakes, Department of Biomedical Engineering and Center for Laser Science and Engineering, University of Iowa, Iowa City, IA

System Design of Materials

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A multi-institutional research program focuses on the fundamental principles underlying strength, toughness, and hydrogen resistance, and the integration of these principles within a systems approach as the basis for design of a new class of ultra-high-strength martensitic steels. Based on a combined SANS, TEM, APFIM, STEM investigation of M2C carbide precipitation, computed thermodynamic scaling factors allow control of competing precipitation reactions to achieve efficient strengthening without embrittlement. Substantial toughness enhancement is demonstrated applying martensitic transformation kinetic theory to predict optimal precipitated austenite dispersions for transformation toughening. Quantum electronic calculations explore the basis for design of boundary composition for enhanced cohesion, and novel impurity-gettering compounds demonstrate major improvements in hydrogen stress corrosion resistance. A Materials Design class has employed these principles in the conceptual design of a hydrogen resistant stainless steel for a Space Shuttle application, demonstrating twice the fracture toughness of existing bearing steels. A new Materials Design Initiative is exploring the extension of this approach to ceramics, polymers, and process foods. Research sponsored by NASA, ONR, ARO, DOE, AFOSR, and NSF.

Processing of Laminated Hierarchical Composites

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Lamination is one of the fundamental approaches used by engineers, and nature, to tailor microstructure for enhanced properties. Motivated by the need for new processing technologies to create engineered microstructures of incompatible polymers, a continuous layer-multiplying technology that will process elastomers, thermoplastics and composites into sheet or film with hundreds or thousands of alternating layers has been developed. With this technology, two polymers are fed from extruders into a feed block as parallel layers, and then into a die element that splits, spreads and recombines the melt. Any number of die elements can be combined in series to produce (AB)n structures. Each die element doubles the number of layers. Numerous examples illustrate how this approach can be used to achieve unusual solid state structure and property characteristics.

Lockup, Chains, and the Delocalization of Damage

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Whether damage is localized or delocalized in a composite, and the composite's fracture toughness when localization occurs can be controlled to a much greater extent than hitherto exploited by properly choosing the composite's internal geometry. Delocalization and high toughness are both favored by building in systematic defects and lock-up mechanisms. Widespread defects make available arbitrarily many sites at which energy may be absorbed by nonlinear behavior. Lock-up mechanisms cause local hardening following local damage, which drives subsequent damage to initiate elsewhere, possibly leading to damage delocalization. In brittle-brittle composites, these mechanisms may be the best hope for achieving toughness values similar to those of alloys. Illustrations are taken from recent research into woven composites with three dimensional reinforcement and new work model composites.

Biomimetic Structures through Chemical Vapor Infiltration

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Hierarchy and Biomineralization - Experimental Approaches

David Kaplan, US Army, Natick RD&E Center, STRNC-YMT, Natick, MA

We have approached the issue of hierarchy and biomineralization from two directions. First, we continue to isolate and characterize macromolecules present in natural shell matrices. A family of proteins has been isolated, characterized by amino acid composition, N-terminal sequencing and glycosylation, and functional studies on calcium binding are ongoing. At the same time, methods to control mineralization at different levels of hierarchy have been investigated using thin film technology. Amino acid-modified diacetylenes have been used as organic templates with calcium carbonate and other salt systems. Modulations in supramolecular template (global geometry, millimeter scale control) influence polymorph selectivity. Calcium binding also influences monolayer molecular area and this is in turn influences polymorph selectivity. We speculate that modulation of supramolecular organization within liquid crystalline phases of cell membranes, coupled with localized pH gradients, could act as modulators of crystal growth in biological systems involved in biomineralization.

Processing of Hierarchically Structured Materials through Self-assembly

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Structure-property relations in biogenic materials provide invaluable guidelines for the structural design of synthetic composites. Three lessons from biogenic composites are central to our efforts in the bioinspired processing of composites: (I) Biogenic composite structures themselves are the building blocks for larger scale composite structures and nested levels of structural hierarchy appear to yield improved properties for particular functions. (ii) Although the principle of hierarchical design has already been applied to synthetic composites, a typical length scale for the smallest level of hierarchy is in the micron range. In contrast, in biogenic composites hierarchical organization always starts on the length scales of 1-100 nm, i.e., nanostructural design is the building block. (iii) Nanostructural design is accomplished through the self-assembly of organics. Inorganic structures are formed as these structurally organized organic surfaces catalytically or epitaxially induce growth of the inorganics. This presentation will focus on the synthesis and processing methods that are used to mimic the structural designs observed in biogenic composites. I will divide the discussion of current research into three areas: (I) nanoscale structures through self-assembly of surfactants; (ii) nanocomposites through scaffolding; and (iii) patterns with the aid of applied fields. In all, the processes used are akin to those found in biogenic systems.

Hierarchical Structures through Stereolithography

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Polymer Melts as Structural Materials: Scaling Relations and Melt-Solid Interfacial Interactions in Processing

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The presentation will describe the most recent advances in the area of polymer materials processing. The unique feature of polymer melts as structural materials is emphasized in terms of their flow instabilities at high rates. In particular, under high stress a strongly entangled melt is capable of undergoing a sudden transition at the melt-wall interface in a capillary flow, producing a large structural discontinuity from weak liquid-solid interactions at the interface to strong chain entanglement in the bulk liquid. As a consequence, a dramatic stick-slip transition occurs at a critical stress corresponding to existence of two widely separated flow rates. The magnitude of the wall slip can be characterized in terms of an extrapolation length b that scales with a molecular distance a through a proportionality constant 2. The constant 2, which reflects the disparity in the dynamic structures between the interfacial chains and the bulk chains, scales strongly with molecular weight and can be extraordinarily large. This relation can predict how behavior of polymer melts in small geometrical dimensions as a function of the polymer entanglement and surface condition.

Ionic Interactions in Polymeric Materials and Hierarchical Structures

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The role of ionic interactions in enhancing mechanical properties of polymeric materials is discussed in terms of hierarchical structures. An introduction of strong, non-directional ionic interactions to polymers leads to the formation of various level of structures. The smallest scale is seen in ionomers, where nano-scale (~1 nm) ionic aggregates are formed and dispersed in the nonionic polymer matrix. These aggregates are responsible for enhanced mechanical properties. The deformation and fracture behavior of glassy ionomers (based on polystyrene or poly (methylmethacrylate)) have been extensively studied in this laboratory. It is found that the formation of ionic cross-links (due to ionic aggregate formation) leads to an enhanced crazing stress, suppressing crazing in favor of shear deformation. These changes in deformation modes are reflected in bulk mechanical properties, such as enhanced tensile and fatigue properties of ionomers.

Larger-scale hierarchical structures can be seen in the blend made of an ionomer and an unmodified polymer, where the micro-scale (~1 μm) ionomer second phase is formed in unmodified polymer matrix due to the difference in polarity between the component polymers. In addition, inside the ionomer phase, nano-scale ionic aggregates (~1 nm) are dispersed. Due to these unique structures, synergistic enhancement in mechanical properties is achieved without losing transparency of the original polymer.

Other types of hierarchical structures in which ionic interactions can be used are polymer matrix composites. In conventional fiber-reinforced composites where micro-scale fibers (~10 μm diameter) are dispersed in the matrix polymer, ionic bonds are utilized to enhance interfacial adhesion between the components. Another example is seen in molecular composites where molecular-scale rigid-rod molecules (~ 1 Å diameter) are dispersed in a coil polymer matrix. Here, too, ionic interactions are used to enhance the dispersity of rod molecules (ionic Kevlar®) into the polar polymer matrix (e.g., poly (r-vinylpyridine)) leads to a change in the deformation mode from crazing to shear deformation. Such a change in the deformation mode is reflected in the effective enhancement in bulk mechanical properties.

Overall, an emphasis is placed on the use of strong ionic interactions in polymeric systems to enhance mechanical properties by producing various level of hierarchical structures.

Toughening Impenetrable Interfaces by Tethered Polymer Chains

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Experiments were conducted to evaluate the effect of polydisperse and monodisperse tethered polymer chains on interfacial toughness. Previously prepared well-characterized polymer chains were tethered to the surface of glass fiber by wet chemical methods. Interfaces were formed by adhering polymer matrix to the glass fiber. Quantitative analysis results suggested that the tethered chains were attached at a sufficiently high areal density to be forced into a stretched conformation, forming a brush-like layer. Toughness was evaluated by measuring the force required to separate the glass fiber from the matrix. In all cases, the presence of the chains was found to increase the interfacial toughness significantly.

The role of tethered chain molecular weight was studied on the glass fiber/polysulfone matrix system with polysulfone tethered chains. Interfacial toughness was observed to increase with tethered chain molecular weight. The toughening is postulated to originate from molecular level interaction of tethered chains and free matrix chains. Part of the interaction is attributed to the softening of the tethered layer profile by the natural polydispersity of the tethered chains.

The role of areal attachment density was studied on the glass fiber/polystyrene matrix system with polstyrene tethered chains. Monodisperse polystyrene chains of a single molecular weight were used, and the attachment density was regulated by blocking techniques applied to the glass surface prior to tethering. Interfacial toughness was observed to increase with lower attachment density in the range studied. This effect is attributed to the reduction in tethered chain stretching with lower attachment densities, a reduction that facilitates interpenetration and interaction of the tethered layer and free matrix chains. The increased interaction, in turn, brings about greater interfacial toughening.

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