

*Nanoscale Structural Design Principles of Biocomposite Exoskeletons As a Guide for New Energy-Absorbing Materials Technologies*

**Team 1 : Energy Absorbing Materials : Multiscale Design and Evaluation of Nanostructured Materials for Ballistic and Blast Protection**

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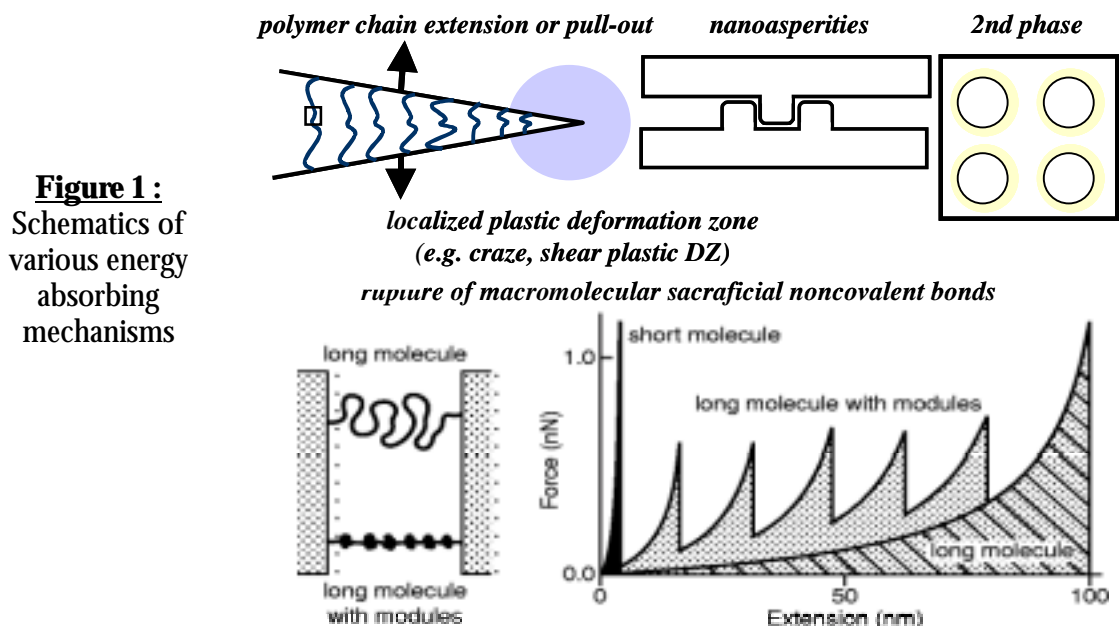
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**I. Background : Structural Design Principles and Energy Absorbing Mechanisms**

From millions of years of evolution, nature has ingeniously figured out innumerate structural design principles to produce multifunctional, and in many cases stimulus-responsive, materials with superior mechanical properties[1-6]. Examples of these include exoskeletons of many invertebrate animals such as mollusks, arthropods (e.g. crustaceans such as crabs, insects), cnidaria (e.g. corals), and structural components of mammals such as turtle shell, rhinoceros horn, bovine hoof horn, deer antlers, elephant tusks, and teeth. Most tough biological materials are complex, hierarchical, multilayered nanocomposites that undergo a wide variety of different energy-absorbing toughening mechanisms at many length scales. Some of these mechanisms in both biological and synthetic composite materials [7-10] are shown in **Figure 1** and include; 1) rupture of "sacrificial" weaker bonds in the macromolecular component (e.g. Mollusk shell nacre), 2) extension, pull-out, and/or ligament formation of a macromolecular component bridging an interface (e.g. Mollusk shell nacre), 3) void formation (e.g. via cavitation of rubber particles in a thermoset composite or stress whitening in semicrystalline polymers) leading to bulk plastic deformation, crack blunting, pinning and branching, 4) localized plastic deformation ahead of a crack tip (e.g. craze or shear deformation zone), 5) microcrack formation (e.g. bone), 6) phase-transformations which take place ahead of a crack tip, 7) viscoelastic dissipation (e.g. crosslinked elastomers), and 8) interacting nanoasperities and mechanical interlocking leading to



**Figure 1 :**  
Schematics of  
various energy  
absorbing  
mechanisms

inelastic strain (e.g. Mollusk shell nacre). Typical values of fracture toughness for various materials are given in **Table 1**.

MATERIAL	$K_{IC}$ (MPa m <sup>1/2</sup> )
metal alloy (steel)	150
mollusk shell	8
rubber toughened epoxy	2.2
soda lime glass	0.8
concrete	0.1-1.4
Si	1
PMMA, PS	1
epoxy, wood	0.5

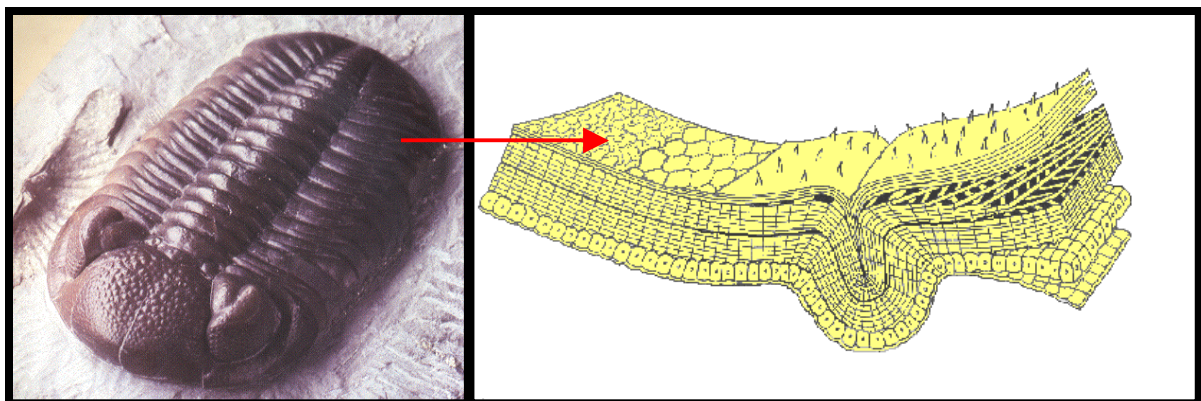
## **II. Research Goals and Interactions with Other ISN Members and Teams**

The goal of this research program is to identify and characterize new, unexploited energy-dissipating mechanisms in tough natural biocomposite exoskeletons so that they can be employed as a guide for new biologically-inspired materials technologies. The project will focus on three major thrust areas; 1) **nanoindentation** to measure the local nanoscale mechanical properties of different morphological components of the composite material, 2) molecular mechanisms of **adhesion** between components and multilayers, and 3) high-resolution **morphological investigations** to determine the molecular origins of energy dissipating processes during deformation and fracture. We plan to run concurrent microscopic and macroscopic mechanical tests in an attempt to interrelate the structure-property relationships at different length scales, as well as employ traditional surface science techniques such as SEM, TEM, optical microscopy, contact angle measurements, FTIR, etc. All of our discoveries and information will be funneled directly into the theoretical simulations of **Boyce and Socrate** on **Team 1** so that these fundamental biological design principles can be employed in the development of the multilayered, synthetic body armor suit. We also plan to interface with **Team 2 Exoskeletons**.

## **III. Detailed Research Plan**

### **III.A. Model Systems**

One model system we plan to study is the arthropod exoskeleton which is a complex multilayered biocomposite as shown in **Figure 2**.

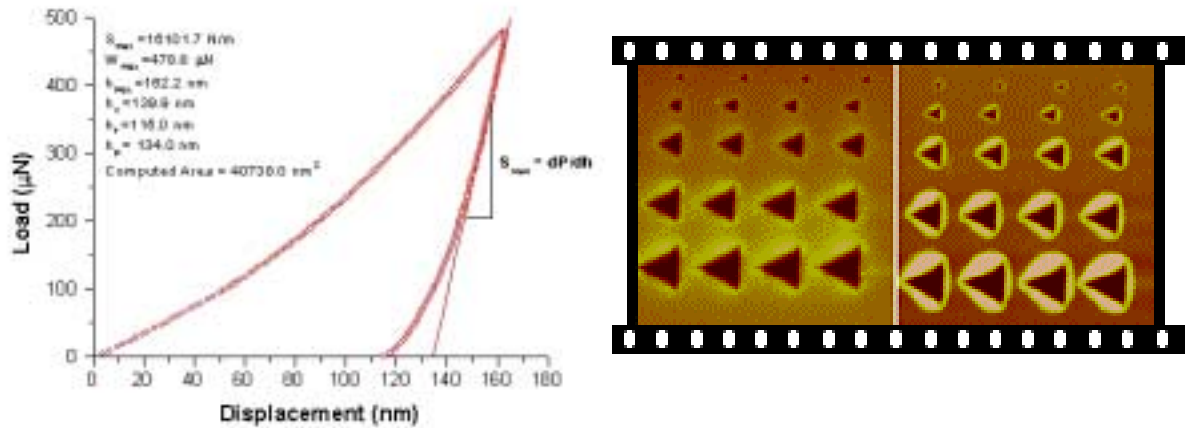


**Figure 2** : (a) <http://paleo.cortland.edu/tutorial/Arthropods/arthropods.htm> (Eldredge (1991)) and (b) <http://www.cals.ncsu.edu:8050/course/ent425/tutorial/integ.html>

One example is the insect exoskeleton that is multifunctional and achieves many properties that are desirable in the synthetic body armor battle suit. It serves not only as a protective covering, but also as a surface for muscle attachment, a water-tight barrier against desiccation and bacterial invasion, a sensory interface with the environment, while simultaneously not compromising the insects' mobility and outstanding locomotion skills. It is a multi-layered composite structure with six functional regions : (starting from outermost layer) : 1) cement layer, 2) oriented layer of wax molecules, 3) epicuticle, 4) procuticle, 5) epidermis, and 6) basement membrane. The outermost **cement** layer provides abrasion resistance and the second innermost **wax** layer serves as the chief barrier to movement of water into or out of the insect's body. The **epicuticle** serves to reduce water loss and block the invasion of foreign matter. The innermost layer of epicuticle is often called the cuticulin layer, a stratum composed of lipoproteins and chains of fatty acids embedded in a protein-polyphenol complex. The **procuticle** consists of microfibers of chitin surrounded by a matrix of protein where thin lamellae with chitin microfibers oriented at a slightly different angle in each subsequent layer. In some parts of the body, the procuticle stratifies into a hard, outer exocuticle and a soft, inner endocuticle. Differentiation of exocuticle involves a chemical process (called sclerotization) that occurs shortly after each molt. During sclerotization, individual protein molecules are linked together by quinone compounds. These reactions "solidify" the protein matrix, creating rigid "plates" of exoskeleton known as sclerites. Quinone cross-linkages do not form in parts of the exoskeleton where resilin (an elastic protein) is present in high concentrations. These areas are membranes- they remain soft and flexible because they never develop a well-differentiated exocuticle. The **epidermis** is primarily a secretory tissue formed by a single layer of epithelial cells. It is responsible for producing at least part of the basement membrane as well as all of the overlying layers of cuticle. The **basement membrane** is a supportive bilayer of amorphous mucopolysaccharides (basal lamina) and collagen fibers (reticular layer) [10].

### III.B. Nanoindentation of Exoskeletons Components and Layers

*Nanoindentation* is an experimental technique whereby a hard, sharp probe tip mounted at the end of a flexible force transducer is indented at constant rate normal to the surface of a softer material and then retracted away from the material surface, giving direct information about local mechanical properties (**Figure 3**). The displacement of the force transducer is measured, for example by a laser beam reflected off the backside of a cantilever beam into a position-sensitive photodiode, and used to measure the force (nN) versus indentation distance or depth (nm) on approach and retract. The technique of nanoindentation is particularly suited for small volume structures and just recently the first measurements on small insect structures have been reported yielding fascinating information on the wing-locking and head-neck articulation mechanisms of beetles[11]. By fits with contact mechanical theories, the following quantitative information of local mechanical properties can be extracted from the force versus indentation depth curves; 1) elastic modulus (via Oliver-Pharr Method), 2) elastic depth, 3) yield force / radius, 4) plastic depth, 5) amount of energy dissipated (mechanical hysteresis), 6) depth and force / radius of any inhomogeneities or minima in the plastic deformation region, and 7) depth and force/radius at fracture. High-resolution AFM imaging will be done at various levels of deformation to investigate the morphology of the indentation area and surrounding region, in order to directly explore elastic and plastic deformation mechanisms at the nanometer level.



(a) (b)  
**Figure 3.** (a) Force versus indentation curve for fused silica

(\*<http://www.hysitron.com/webpage2/HomePage.htm>) (b) Schematic of a nanoindentation experiment on diamond-like carbon thin films using three different forces (23, 34, and 45µN) with four indents made at each force. Each film was indented using the same force and cantilever in order to compare hardness. 500nm scan. (\*Downloaded from : <http://www.di.com/cgi-bin/DIgallery.exe/NI3onDLC.gif>)

III.C. Adhesion Mechanisms Between Exoskeleton Composite Layers

The macromolecular adhesives at biological interfaces play a critical role in the function and durability of the structure. Recently, it has been suggested that multiple sacrificial, noncovalent bonding interactions in these adhesive glue are a critical component in promoting energy dissipation and most likely serve other unknown roles in the structure as well [8]. HRFS experiments will be conducted between various multilayers of the biocomposite structures, which are run at constant rate normal to the sample surface and then retracted away from the surface. However, for measurement of intersurface interactions (e.g. van der Waals, hydrophobic, H-bonding, electrostatic, etc.), the spring constant of the cantilever force transducer will be chosen to be much less than the stiffness of the substrate so no indentation takes place and instead, what is measured is force (nN) versus probe tip-surface separation distance (nm).

III.D. High Resolution Morphological Investigations of Deformation and Fracture

In this subtopic of the proposed research, the deformation and fracture morphology of the exoskeleton layers will be directly visualized at the nanometer scale. Changes in morphology, including plasticity, will be investigated with increasing deformation and correlated to distinctive points on the load versus indentation curves. Fracture surfaces will be imaged noting the appearance of crack fronts, edges, and the zone ahead of the crack tip.

## **IV. Laboratory Facilities and Equipment**

### **IV.A. Ortiz Polymer Mechanics Laboratory**

- Experimental facilities include a chemistry / biology laboratory (MIT, RM 12-065) and a mechanical testing laboratory (MIT, RM 13-5037).
- *Digital Instruments* NanoScope IIIA System Controller with Multimode Atomic Force Microscope (AFM)
- 1-D Molecular Force Probe (MFP) by *Asylum Research, Inc.*
- *I.C. Adams<sup>TM</sup>* Nanomechanics Force Spectroscopy Simulation Software
- *Zeiss, Inc.* Axioskop 20 optical microscope with transmitted and reflected light, differential interference contrast, cross-polarizers, and incident light fluorescence
- *Kodak* Digital Science Microscopy Documentation System 100 (MDS 100) for in-situ observations of deformation and fracture.

### **IV.B. Centralized Facilities Available**

- Micro/Nanoindenter (*MicroMaterials, LLC*): This indenter is capable of cyclic and high temperature (<1000C) indentation, for a maximum applied load of 20 N or a maximum displacement of 30 microns.
- Nanoindenter (*Hysitron, Inc.*): This nanoindenter features in situ imaging and AFM imaging of indentations, for a maximum applied load of 30 mN or a maximum displacement of 5 microns.
- 3-D Molecular Force Probe (MFP) by *Asylum Research, Inc.*
- Scanning force microscope (*Quesant*): This stand-alone AFM images an area of 90 x 90 microns, in constant or intermittent contact modes, and can profile surface heights of up to 10 microns.
- Light microscope (*Nikon*): This high magnification light microscope (1000x) can be used to map samples for further analysis, and can acquire images digitally for archival.
- Table-top electromechanical universal (*Instron*): This small tension/compression apparatus can be used for low cycle fatigue and standard uniaxial testing of small or thin specimens.

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