STATEMENT OF WORK FOR PROJECT 1.6

Title of Project  Multiscale Design and Evaluation of Nanostructured Biological and Synthetic Composite Materials for Ballistic and Blast Protection

Principal Investigator(s)  Christine Ortiz

Research Team No  1

Impacted Capability Areas: Protection___X ; Performance Enhancement____; Injury Intervention & Cure_

Objectives:
The objective of this project is to discover new and more effective energy-dissipating deformation mechanisms and to understand their relationship to design principles in nanostructured biological and synthetic composite materials. The specific aims are to conduct macro- and microscale tests for impact resistance on a broad array of materials including: 1) naturally tough biological nanostructured composite materials (to identify the world's toughest biological composite material), 2) new synthetic nanocomposite materials produced by our collaborators on Team 1, and 3) current commercially available synthetic soft and hard body armours. Based on these results, we will then focus on investigating the nanoscale structure-deformation relationships of a few select model systems via our expertise in novel nanomechanical and high resolution imaging techniques. Lastly, we will employ these fundamental scientific laws to aid in the design and advancement of new synthetic biologically-inspired body armour technologies.

Rationale:
Through millions of years of evolution, nature has ingeniously figured out innumerate nanoscale structural design principles to produce multifunctional, and in many cases stimulus-responsive, materials with superior mechanical properties. Most tough biological materials are complex, hierarchical, multilayered nanocomposites that undergo a wide variety of poorly understood toughening mechanisms at many length scales. Some of these include; rupture of "sacrificial" weaker bonds, extension, pull-out, and/or ligament formation of a macromolecular component bridging an interface, void formation, bulk plastic deformation, crack blunting, pinning and branching, localized plastic deformation ahead of a crack tip, viscoelastic deformation, and interacting nanoasperities and mechanical interlocking. Our studies will be able to identify and understand such energy-absorbing mechanisms and provide fundamental nanostructure-property laws to be used as a design guide for new synthetic, biologically-inspired soldier protection and survivability materials technologies. Such studies on the new synthetic nanocomposite materials produced by our collaborators on Team 1 will also create a strong foundation that will be critical for rapid improvement and refinement.

Methods of Approach:
Materials. A broad array of natural materials will be studied such as invertebrate exoskeletons, cnidaria (e.g. corals), shells (e.g. turtle, armadillo, abalone), hoof, horn, dermally ossified body armour plates (e.g. Ankylosaurs), and armoured fish plates (e.g. Gasterosteus-Aculeatus), as well as new synthetic macromolecular architectures (Project 1.1, Swagger, Thomas), nanorelief networks, self-assembled trusses (Project 1.2, Thomas, Boyce, Swagger, Socrate), hierarchical nanocomposites (Project 1.3, Thomas, Boyce), artificial silk (Project 1.4, McKinley, Hammond), and multilayered extrusions (Project 1.8, Cohen). A few commercially available soft body armours will also be tested such as Kevlar®, Twaron®, Spectra®, and Dyneema® fiber-based bullet proof vests.

1) A number of different macro and micro-scale quasistatic impact and indentation tests will be conducted depending on the particular material under investigation such as pendulum-type Izod (ASTM D256, D3420), Charpy (ASTM D6110), and tensile (ASTM D1822) tests, drop weight-type Gardner dart test (ASTM D-3029, ASTM D1709, D5420, D5628), or instrumented impact machines. In an instrumented impact test, the falling dart's tip or the pendulum's hammer is fitted with a load cell and the force-time data during the impact is stored by a high-speed data-acquisition system which can then be used to generate data curves showing force, energy, velocity, and deformation versus time. By analyzing these curves, one can learn the force, energy, and deformation necessary to initiate a crack and then to cause total failure, the rate sensitivity of a material to impact loading, and the temperate of a material's transition from ductile to brittle failure mode.

2) The technique of nanoindentation will be employed to measure the local nanoscale mechanical properties of different morphological components/layers of the biocomposite material. Nanoindentation is an
experimental technique whereby a hard, sharp nanosized probe tip mounted at the end of a force transducer is indented and then retracted at constant rate normal to the surface of a material, giving direct information about local nanoscale mechanical properties. 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 record the force (nN) versus indentation distance or depth (nm). By fits with contact mechanical theories, quantitative values of local mechanical properties will be extracted such as; elastic modulus and depth, yield force and depth, amount of energy dissipated during deformation cycle (i.e. mechanical hysteresis), fracture depth, force, and energy. These values for nanoscale mechanical properties will provided to Boyce, Socrate to employ in their theoretical simulations.

3) **High-resolution morphological investigations** will be carried out using the technique of *atomic force microscopy* (AFM) imaging to determine the molecular origins of energy dissipating processes during deformation and fracture. Contact, tapping, and phase imaging modes of AFM will be performed 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 scale. In this subtopic of the proposed research, the deformation and fracture morphology of the biocomposite layers will be directly visualized. 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. Traditional lower resolution microscopy will also be employed such as scanning electron microscopy, transmission electron microscopy, and transmitted and cross-polarized optical microscopy.

4) The **molecular mechanisms of adhesion** between various nanoscale morphological components and layers will be investigated via the technique of *high resolution force spectroscopy* (HRFS). Compared to nanoindentation, HRFS employs a nanosized probe tip at the end of a much softer force transducer to measure surface forces (e.g. van der Waals, hydrophobic, H-bonding, electrostatic, etc.) so that no sample indentation takes place and instead, what is measured is force (nN) versus probe tip-surface separation distance (nm). HRFS will yield information about the macromolecular adhesives at biological interfaces that play a critical role in the mechanical function and durability of the structure. For example, in many cases, multiple sacrificial, noncovalent bonding interactions in these adhesive glues are a critical component in promoting energy dissipation.

**Key Personnel:**

Ben Bruet, RA, 1st year, (Ortiz group)

**Project Schedule With Milestones:**

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<tr>
<th>Year 1</th>
<th>Year 2</th>
<th>Year 3</th>
<th>Year 4 &amp; Beyond</th>
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<td>• Identify the world’s toughest known biological composite material and compare to synthetic materials</td>
<td>• To understand why it’s the world’s toughest biological composite material, i.e. nanoscale structure-property relationships via nanomechanics &amp; HR morphological investigations</td>
<td>• To create a synthetic analogue / prototype of world’s toughest biological composite material</td>
<td>• Proof of concept</td>
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<td>• Technology transitioning</td>
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<td>• Scale-up</td>
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**Expected Benefits:**

This project will provide an across-the-board evaluation of materials for Team 1 and act as a constant source of new ideas and directions for synthetic design. It will provide a fundamental scientific understanding through novel nanomechanical techniques such as nanoindentation, HRFS, and AFM and thus, create a strong foundation for rapid improvement and refinement of newly developed technologies. It is expected that in YR 4 a new product will be ready to transition to an industrial partner for further development, proof of concept testing, scale-up, etc.