SYMPOSIUM Y

Mechanical Properties of Bio-Inspired and Biological Materials

November 29 - December 2, 2004

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* Invited paper

SESSION Y1: Mechanical Properties of Bio-Inspired and Biological Materials I
Chairs: Kalpana Katti and Christopher Viney
Monday Morning, November 29, 2004
Room 205 (Hynes)

8:30 AM *Y1.1
Biomechanics in Functional Tissue Engineering. Kai-Nan An, Division of Orthopedic Research, Mayo Clinic College of Medicine, Rochester, Minnesota.

Significant advances have been made in tissue engineering over the past decade, though major challenges remain in repair or replacement of tissue that serves a predominantly biomechanical function. Two biomechanical aspects need to be addressed. First, the in vivo loading environment encountered by the native and repaired/replaced tissue, and second, the material properties of the native and replaced tissue. The technology available for assessing each of these and the significance of the information obtained will be addressed using examples in musculoskeletal systems. Tissue and organs experience complicated loading during normal physiological activities or pathological conditions. Numerous experimental technologies have been developed for directly assessing such loading and deformation. Imaging technology has opened the door for noninvasive assessment of the loading environment in vivo. Analytic modeling has been extensively developed and validated, which provides useful and powerful tools in this investigation. It enables the estimation of loading and the simulation of activities associated with potential injury. The analytic model also provides more insight into the mechanism of loading and spatial and temporal variations of the loading in a more precise manner. Parametric analysis of the model facilitates optimal design of the tissue engineered construct and treatment procedures. Information on the in vivo loading environment defines the functional requirement or mechanical thresholds that normal tissue encounters. Correlation of loading information with the tissue composition and morphology has provided important clues as to how the tissue models or remodels when subjected to mechanical manipulation and stimulation, such as that using bioreactors before surgery or a rehabilitation program after surgery. Material properties can be used to predict the mechanical response of tissue under load. Inhomogeneous, nonlinear, anisotropic and viscoelastic characteristics of biological tissues make mechanical assessment challenging. Structural properties of tissue and engineered constructs incorporate both material and geometric properties, including the morphology and microstructure. This parameter could be directly related to the functional performance of the tissue engineering procedure and construct. Material properties, on the contrary, are valuable to the understanding of the physical properties of tissue. Finally, when considering cellular activity, the tissue properties might not be appropriately treated as averaged values considered in the classic continue mechanics. Micro- and nano-technologies are being developed for characterizing the physical properties of the molecules which directly interact with the cells. Combining the material property information with the loading encountered, the baseline data expected in design and the safety factor required under both subfailure and failure conditions could be established.

9:00 AM Y1.2
Examination of the Dynamic Mechanical Properties of Tissue Engineering Scaffolds. Catherine Klapperich[2,1] and Heather Kauth[1]; [1]Department of Biomedical Engineering, Boston University, Boston, Massachusetts; [2]Manufacturing Engineering, Boston University, Boston, Massachusetts.

Scaffolds of both natural and synthetic materials have been widely utilized to provide a three dimensional environment for cell growth. The characteristics of these scaffolds play a vital, but sometimes ambiguous, role in tissue engineering constructs. Collagen-glycosaminoglycan matrices have been used clinically as artificial skin implants. Previous research in our laboratory on this model has shown that gene expression is regulated by mechanical stress applied to the matrix. In this work we begin the process of quantifying the effects of mechanical stress and preparation technique on a matrix comprised of type I collagen and chondroitin-6-sulfate. Cyclic modes of compression were applied to the matrices using a dynamic mechanical analyzer at 37 degrees Celsius and retrofitted with 5% carbon dioxide gas flow. All samples were tested hydrated in either simulated body fluid or PBS. Storage and loss modulus values as a function of frequency data are presented. Mechanical tests were performed on collagen-GAG meshes both seeded with human dermal fibroblasts and not seeded with cells. Further work includes gene expression analysis of the cells on the seeded matrices in order to identify differential gene expression induced by mechanical loading.

9:15 AM Y1.3
Biopolymeric Bone Graft Substitute for the Spine. Stephen A. Doherty[1], David D. Hile[1], Qi Liu[2], Marie Shea[2] and Wilson C. Hayes[2]; [1]Cambridge Scientific, Inc, Cambridge, Massachusetts; [2]Orthopaedic Biomechanics Lab, Oregon Health and Sciences University, Portland, Oregon.

Bone is second only to blood in the number of transplant procedures performed. Approximately one million bone-grafting procedures are performed annually worldwide, with approximately 50% being performed in the United States. Spinal fusion is the most common type of grafting procedure, with more than 250,000 procedures performed annually. In a typical process, autologous bone, the"gold standard", is used to construct the fusion site. However, the limited supply of autograft, the variable quality of available autograft, and concerns over the safety of allograft has fueled the search for synthetics that may be used to augment or replace autograft in bone grafting procedures. Bone graft substitutes are evaluated based on their ability to provide immediate structural support while encouraging bone ingrowth as fusion progresses. A biopolymeric scaffold can add dimensional stability to autograft bone and maintain the osteoinductive properties of the autograft via its ability to support the volume and shape of the fusion site. The use of a bioabsorbable osteoconductive bone graft substitute would allow for immediate stabilization, while allowing for replacement by new bone growth as the polymer degrades. The proposed bone graft substitute is based on the biodegradable polymer poly(propylene fumarate-co-fumaric acid) (PPF). PPF, is an unsaturated polyester that can be crosslinked in the presence of effervescent and osteoconductive fillers, as well as autograft bone, and cured in situ yielding a porous bone-like scaffold in intimate contact with host tissue. The use of a degradable biopolymeric scaffold could, at least, extend the working volume of autograft without compromising its osteoconductive properties and, at best, improve upon the mechanical and bioactivity properties of the graft material as graft consolidation occurs. The fact that the proposed graft substitute sets, or cures, in a surgical relevant timeframe would also be advantageous in the placement of fusion instrumentation, such as screws, cages, and plates. Previous studies have demonstrated the ability of the bone graft substitute to increase the working volume of bone in a rat tibial defect model. The current study evaluates the suitability of the bone graft substitute material to support spinal fusion, as defined by mechanics appropriate for immediate stabilization at placement and continuing stabilization of the polymer-bone construct over the course of the fusion process concomitant with the maintenance of porosity permissive for cellular ingrowth. The results of the evaluation of bone graft substitute as related to sensitive formulation variables based upon initial and temporal morphological and mechanical outcomes will be presented.

9:30 AM Y1.4
Carbon Nanotube Reinforced Bombyx Mori Nanofibers By The Electrospinning Process. Jonathan Ayutsede[1], Milind Gandhi[2], Sachiko Sukigara[3] and Frank Ko[1]; [1]Materials Science and Engineering, Drexel University, Philadelphia, Pennsylvania; [2]School of Biomedical Engineering, Sciences and Health Systems, Drexel University, Philadelphia, Pennsylvania; [3]Faculty of Education and Human Sciences, Niigata University, Niigata, Japan.

Silk has been in use for over 5000 years as high fashion textiles and for surgical sutures. The triangular shape and 10-20 μm diameters of Bombyx Mori fibers remain unchanged over the years. In this study we examine the scientific implication and application potentials of reducing the diameter to the nanoscale, changing the triangular shape of the fiber and reinforcing the fibers with carbon nanotubes by the electrospinning process. Fiber diameters as low as 7 nm with circular cross-section and smooth surfaces have been fabricated. The electrospinning process is also able to preserve the natural conformation of silk (random and β-sheet). However, the mechanical properties of the electrospun fiber were lacking in comparison with the natural fiber due to the processing steps involved. The availability of carbon nanotubes (CNT) which exhibit exceptional mechanical properties provide attractive material design options to tailor the mechanical properties of the silk for various applications.Consequently, by co-electrospinning CNT with silk fibroin, a nanocomposite may be fabricated to yield multifunctional strong and tough nanofibers. Regenerated silk fibroin in carbon nanotube-formic acid solution was electrospun and the morphological, chemical, structural and mechanical properties of the nanofiber was examined by field emission environmental scanning microscopy, Raman & Fourier Transform Infra Red Spectroscopy, Wide Angle X-Ray Diffraction and micro tensile tester respectively . We have shown for the very first time, the feasibility of fabricating a nanocomposite combining the bioactivity of silk and structural reinforcement of CNT through the electrospinning process. The spinning dope was prepared by dispersing CNT in formic acid and incrementally adding silk to aid the dispersion by preventing agglomeration of the nanotubes through steric, hydrophobic and electrostatic effects. The conformation of the silk is conserved as shown by the FTIR results and there is a 2 % increase in the crystallinity index. The mechanical properties of the electrospun CNT reinforced fibers show significant improvement with increases in Youngs modulus up to 464 % in comparison with electrospun non-reinforced fibers. Taking advantage of the biocompatible nature of silk, we envision the development of a new family of multifunctional protein-based nanofibers.

10:15 AM Y1.5
Spectrin-Level and Continuum Modeling of Mechanical Response of Human Red Blood Cells. Ming Dao[1], Ju Li[3] and Subra Suresh[1,2]; [1]Dept of Materials Science & Engineering, MIT, Cambridge, Massachusetts; [2]Division of Biological Engineering, MIT, Cambridge, Massachusetts; [3]Dept of Materials Science & Engineering, Ohio State University, Columbus, Ohio.

The large deformation elasticity characteristics of human red blood cells are known to influence strongly their biological functions and the onset, progression and consequences of a number of human diseases. The mechanics of the whole human red blood cell (RBC) subjected to large deformation by optical tweezers was studied in detail at the continuum level by finite-element modeling as well as at the spectrin level by molecular dynamics and conjugate gradient energy minimization methods. The mechanical responses of the cell during loading and upon release of the optical force are then analyzed to extract the elastic properties of the cell membrane by recourse to several different constitutive formulations of the elastic and viscoelastic behavior with fully three-dimensional model constructions. A parametric study of various geometric, loading and structural factors is also undertaken in order to develop quantitative models for the mechanics of deformation by means of optical tweezers.

10:30 AM Y1.6
Role of molecular interactions at polymer-mineral interfaces on mechanical response. Rahul Bhowmik, Kalpana S. Katti and Dinesh R. Katti; Civil Engineering, North Dakota State University, Fargo, North Dakota.

Polymer-hydroxyapatite nanocomposites are widely used as bone replacement materials. The mechanical responses of these nanocomposites are known to be influenced by molecular interactions at mineral-polymer interface. Molecular modeling of these interactions is an area of current interest but force field parameters of such dissimilar molecules are not available for a common force field. Also, parameters for several commonly used force fields are not available in the literature for hydroxyapatite. Recently a unique force field was described in literature that represents the structure of hydroxyapatite reasonably well. Yet the applicability of this force field for studying the interaction between dissimilar materials (such as mineral and polymer) is limited as there is no accurate representation of polymer. CVFF (consistent-valence-force-field) is a commonly used force field for which parameters of many material systems are available. We have obtained the parameters of CVFF for monoclinic hydroxyapatite from the known potential energy function of apatites and experimentally obtained infrared spectra. Validation of simulations is done by comparison of computationally obtained unit cell parameters, vibrational spectra and different atomic distances with experimentally obtained XRD and FTIR data. Ab initio methods are used to obtain interfacial parameters for polymer mineral interactions. This study represents molecular modeling of polymer-mineral interfaces.

10:45 AM Y1.7
Evaluation of Deformation Mechanisms at Mineral-Protein Composite Interface using Steered Molecular Dynamics Simulations. Dinesh R. Katti, Pijush Ghosh, Steven Schmidt and Kalpana S. Katti; Civil Engineering, North Dakota State University, Fargo, North Dakota.

Mineral-organic interfaces and interphases are common in many biomaterials and also biological materials. The understanding and modeling of mechanical response of such interfaces are important issues in the design of biomaterials. In this work, a model mineral-organic system consisting of montmorillonite and amino acids is studied. Montmorillonite, a swelling clay mineral has drawn considerable attention in the field of nanocomposites. The intercalation and exfoliation of montmorillonite as a result of separation at the interlayers allows for formation of nano inclusions in a nanocomposite. Clay nanocomposite composed of montmorillonite and synthetic polymers are used as structural materials. Clay composite with biopolymer on the other hand have potential applications as biosensors, composites and for uses in pharmaceutical industry. Biopeptides or more specifically proteins could be a very effective inclusion in the montmorillonite interlayer. In this work, we study the behavior of the mechanical properties of the montmorillonite interlayer in the presence of protein. Lysine and arginine, the two commonly found positively charged amino acids are used in this study. The behavior of the interlayer is studied both under tension and compression. Our simulations using steered molecular dynamics of the mineral interlayer with amino acids indicate significantly different mechanical properties under compression and tension stress paths. The response under tensile stress path was found to be significantly stiffer than in compression. Based on the mechanical responses, the orientation of the amino acids during loading and the arrangements of the angles and dihedrals observed under tensile and compressive stress paths, we have propose the deformation mechanisms of the mineral-protein composite and its interface. This paper deals with development of model, selection of amino acids, simulation details and interpretation of results.

11:00 AM Y1.8
Atomistic and Continuum Studies of Flaw Tolerant Nanostructures in Biological Systems. Huajian Gao, Markus J. Buehler, Baohua Ji and Haimin Yao; Max Planck Institute for Metals Research, Stuttgart, Germany.

Bone-like biological materials have achieved superior mechanical properties through hierarchical composite structures of mineral and protein. Gecko and many insects have evolved hierarchical surface structures to achieve superior adhesion capabilities. What is the underlying principle of achieving superior mechanical properties of materials? Using joint atomistic-continuum modeling, we show that the nanometer scale plays a key role in allowing these biological systems to achieve such properties, and suggest that the principle of flaw tolerance may have had an overarching influence on the evolution of the bulk nanostructure of bone-like materials and the surface nanostructure of gecko-like animal species. We illustrate that if the characteristic dimension of materials is below a critical length scale on the order of several nanometers, Griffith theory of fracture no longer holds. An important consequence of this finding is that materials with such nano-substructures become flaw-tolerant, as the stress concentration at crack tips disappears and failure always occurs at the theoretical strength of materials, regardless of defects. The atomistic simulations complement continuum analysis and reveal a smooth transition between Griffith mode of failure via crack propagation to uniform bond rupture at theoretical strength below a nanometer critical length. Below the critical length for flaw tolerance, the stress distribution becomes uniform near the crack tip. Our modeling resolves a long-standing paradox of fracture theories. These results have important consequences for understanding failure of small-scale materials. We further show that the nanoscale sizes allow the spatula nanoprotrusions in Gecko to achieve optimum adhesion strength. Strength optimization is achieved by restricting the relevant dimension to nanometer scale so that crack-like flaws do not propagate to break the desired structural link. Additional investigations focus on shape optimization of adhesion systems. We illustrate that optimal adhesion can be achieved when the surface of contact elements assumes an optimal shape. The results suggest that optimal adhesion can be achieved either by length scale reduction, or by optimization the contact shape. We discuss these results in the perspective of adhesion systems found in biological systems.

SESSION Y2/R2: Joint Session: Nanomechanics and Tribology of Biological Material
Chairs: David Bahr and George Pharr
Monday Afternoon, November 29, 2004
Room 202 (Hynes)

1:30 PM *Y2.1/R2.1
Coaxial Single Molecule Fluorescence and Scanning Probe Microscopies: Applications to the Study of Soft Materials. Christopher M. Yip, Chemical Engineering / IBBME, University of Toronto, Toronto, Ontario, Canada.

We recently developed an integrated imaging platform that combines single molecule evanescent wave fluorescence imaging (and spectroscopy) with in situ scanning probe microscopy. The advantages, challenges, and potential represented by this coupled tool will be described in the context of the structure-function characteristics of nanostructured biomaterials and thin lipid films.

2:00 PM Y2.2/R2.2
Nanomechanical and Microstructural Features of Silk Films. Donna M. Ebenstein[1], Jaehyung Park[2], David L. Kaplan[3] and Kathryn J. Wahl[1]; [1]Code 6176, U.S. Naval Research Laboratory, Washington, District of Columbia; [2]Chemical Engineering, Tufts University, Medford, Massachusetts; [3]Biomedical Engineering, Tufts University, Medford, Massachusetts.

The high strength and elasticity of silk fibers has many researchers trying to create synthetic fibers or coatings from silk proteins that have comparable mechanical properties to the native fibers of silkworms or spiders. Research has shown that silk fibroin protein can have two distinct microstructures: a less structurally organized silk I phase and a silk II phase made up of more highly structured beta-sheets. When silk fibers are spun by silkworms or spiders, the

silk has a large percentage of the silk II structure, which is thought to impart much of its high strength. In this study, nanoindentation was used to investigate the mechanical properties and microstructure of silk films made from silkworm fibroin protein under a variety of different processing techniques. 12 different specimens were tested: 5 samples which underwent combinations of methanol, water, and stretching treatments; a control specimen that underwent none of those 3 treatments; and the same 6 samples following an enzymatic etching treatment. The methanol, water, and stretching treatments were investigated as techniques to increase the silk II component of the films, and hence improve their mechanical properties. The etching was expected to selectively digest the less organized silk I protein conformation, to reveal silk II structures. Two different nanoindentation techniques were used to study these films: (1) traditional quasi-static indentation, and (2) dynamic stiffness imaging. The quasi-static nanoindentation data showed that the silk films (before etching) ranged in modulus from 6.5 to 9.5 GPa, with the control specimen having a modulus of 7.6 GPa. Methanol and water treatment both resulted in increased moduli relative to the control film (> 9 GPa). Stretching alone had no measurable effect on the mechanical properties relative to the control film, but combining stretching and methanol treatment produced the sample with the lowest modulus of this group (6.5 GPa). Etching had a variable effect on the mechanical properties of the films, with the methanol-treated films showing the least change in modulus. Dynamic stiffness imaging provided information on the microstructure of the different silk films. For example, the dynamic stiffness images revealed an alignment of microstructure in the direction of strain for all the stretched specimens. In addition, dynamic stiffness revealed changes in structure after etching in many of the films. In this paper we will show how different processing treatments during silk film production can change the microstructure and mechanical properties of the resultant films.

2:15 PM Y2.3/R2.3

Nanoscale Characterization of Physisorbed Biofilms.
Michelle Emma Dickinson and Adrian B. Mann; Ceramics and Materials Engineering, Rutgers The State University Of New Jersey, Piscataway, New Jersey.

The properties and function of physisorbed proteinaceous biofilms are a major economic, ecological and biomedical issue. They are important in applications as diverse as osteointegration of biomaterials and biocorrosion of ship hulls. In this study nanoindentation and AFM have been used *invitro* to examine the acquired salivary pellicle formed *invivo* on dental enamel. This is an organic biofilm formed by the physisorption of proteins and carbohydrates on to the surface of dental enamel exposed to the oral environment. The pellicle has several key roles in oral physiology including lubrication and reduction of friction between teeth during mastication, as well as chemical protection of the enamel against acidic solutions. The mechanical properties, growth, structure and morphology of pellicle grown on clean natural and artificial ceramic surfaces has been studied. It was found that complete coverage of the enamel surface occured within the first few minutes of exposure, with the maximum thickness of 200-500nm achieved within 2 hours. The morphology of the pellicle surface was found to be a dense arrangement of globular shapes covering the whole surface of the tooth. Furthermore we have examined the effects of dietary agents such as tannins on the pellicle's properties. Tannins are phenolic compounds found commonly in food and beverages. They have a strong interaction with proteins causing a dark staining of the pellicle layer which then creates a stained effect on the teeth. The mechanical properties of pellicles after tannin treatment show a sizeable difference as revealed by changes in the nanoindentation force displacement curves. Using nanoscale dynamic mechanical analysis (nanoDMA) the viscoelastic properties of the pellicle have been studied. This has confirmed that there are substantial variations in the storage and loss modulus of pellicle with increasing exposure to tannin containing solutions. These changes in viscoelasticity impinge directly on the pellicle's performance as a lubricant and also the ease with which it can be removed using an abrasive dentrifice (toothpaste).

2:30 PM Y2.4/R2.4

Natural Contact Processes Emulated by Nanoindentation.
Susan Enders, Nato Barbakadse, Stanislav N. Gorb and Eduard Arzt; Max-Planck-Institute for Metals Research, Stuttgart, Germany.

Natural anti-adhesive surfaces are of great interest since they may serve as a model for artificial surfaces or surface treatments. Surfaces with anti-adhesive properties are, for example, one mechanism carnivorous plants use to catch their pray. In addition to diverse surface structures, layers of wax crystalloids prevent proper attachment of the insect's feet and thus their escape from the deadly trap. There are several hypotheses about the anti-attachment function of the waxy coatings. It may be due either to their chemical or wetting properties or their mechanical stability or instability, respectively. Weak crystalloids will break during contact whereas a surface with stable crystalloids results in a rough surface and may cause a decrease of the contact area between the plant surface and insect pads. With the help of selective local deformation tests performed using instrumented nanoindentation we simulated the contact formation of an insect foot and thus determined the mechanical stability of crystalloids. During the tests the contact stiffness as well as the force and displacement were recorded and from this data an estimation on the stability of the wax crystalloids was drawn. The results obtained were then compared with insects of different weight and attachment pad size.

2:45 PM Y2.5/R2.5

Nanomechanical Testing of Hydrated Biomaterials: Sample Preparation, Data Validation and Analysis.
Catherine Klapperich[2] and Jessica Kaufman[1]; [1]Department of Biomedical Engineering, Boston University, Boston, Massachusetts; [2]Department of Manufacturing Engineering, Boston University, Boston, Massachusetts.

Implants, tissue engineering scaffold materials, drug delivery and bio-micro electromechanical systems (BioMEMs) all use polymer or hydrogel materials. These applications require both mechanical performance and successful integration of the material into a biological environment. Mechanical strength, storage and loss moduli, wear resistance, surface adhesion properties and surface chemical composition are all critical in biomedical device design and can be determined using nanoindentation. The difficulty of obtaining large samples of specialized materials and the complexity of testing soft materials in traditional materials testing apparatus, make nanoindentation an attractive alternative. Our previous research using nanoindentation to measure the surface mechanical properties of non-hydrated polymers led to improvement in nanoindentation testing protocols. One of the major challenges in using this technique for soft materials is maintaining and controlling hydration of the materials during the test. Here we describe the design of a microfluidic platform for nanoindentation that facilitates continuous hydration of hydrogel samples and high throughput nanomechanical testing. We will show data from both stress relaxation and creep experiments on synthetic, hydrated biomaterials and tissues. We are also able to show the mechanical changes of these materials as a function of hydration levels and pH changes at the nano and microscale. In addition, we show data to validate the materials properties determined from nanomechanical testing by complementary testing using macro and nano dynamic mechanical analysis. Finally, data from both test methods are fitted to phenomenological models for viscoelastic materials.

3:30 PM *Y2.6/R2.6

The effect of TGF-βbeta and glucocoticoid signaling on local mechanical properties of mouse bone.
Mehdi Balooch[1], Sally J. Marshall[1], Grayson W. Marshall[1], Guive Balooch[1], Nancy Lane[2] and Wei Yao[2]; [1]UCSF, San Francisco, California; [2]SFGH, San Francisco, California.

Growth factor and hormone signaling can drastically affect the process of hard tissue formation, e.g. signaling molecules that have a large affect on bone formation include Transforming Growth Factor-β (TGF-β) and Glucocorticoids(GC). TGF-β has a vital and complex role in bone. TGF-β binds its cell-surface receptor to activate Smad3, a transcription factor that regulates the expression of defined genes, that determine osteoblast differentiation. However the effect of TGF-β on bone matrix quality is less clear. Excess glucocorticoids (GC) frequently leads to osteoporosis which is associated with increased fracture risk. This study assessed the effect of altered TGF-β signaling and GC excess on the intrinsic mechanical properties of mice bone. For the GC studies, we administered 1.4 mg/kg prednisolone to 6-month-old Swiss-Webster mice for 21 days. For TGF-β studies, transgenic mouse models with altered TGF-β signaling, ranging from 16-fold (D4 mice) and 2.5-fold (D5 mice) overexpression of TGF-β in bone, to decreased TGF-β signaling due to expression of a dominant negative TGF- receptor in bone (E1 mice) and targeted deletion of the Smad3 gene (Smad3 -/- and Smad3 +/- mice) were evaluated. Atomic force microscopy (AFM)/nanoindentation with stiffness mapping capability was utilized to assess the local bone quality. Raman microspectroscopy was performed to evaluate mineral and collagen content locally. Mice treated with GC had decreased serum osteocalcin in the lumbar vertebrae (LVB) compared to GC naive mice. This change in GC treated mice was accompanied by decreased bone formation (35%) and increased osteocyte apoptosis compared to GC naive controls (56%). Compared to GC naive mice, elastic modulus assessed across the trabecular bone regions was significantly reduced around osteocyte lacunae in GC treated mice (67%), independent of osteocyte apoptosis. Raman microspectroscopy of bone matrix/mineral around the osteocyte lacunae yielded a significant decrease in phosphates/organic content in GC treated mice compared to GC naive (36%). The findings provide evidence that GC-induced bone fragility could arise from changes associated with the osteocyte lacunae that alter bone strength Mice with elevated TGF-β signaling had on the average up to 23% lower elastic modulus and hardness relative to wild-type littermates. However, stiffness mapping revealed the existence of significant texturing in elastic modulus, ranging from 15 to 40 GPa. In contrast, mice in which TGF-β signaling was impaired (E1, Smad3 +/-, Smad3 -/-) had up to 54% increased elastic modulus and hardness, with no detectable texturing in elastic modulus. Though both have decreased TGF-β signaling, E1 mice are osteopetrotic whereas Smad3 -/- mice are osteopenic. In conclusion, we have provided evidence that growth factor and hormone signaling define bone intrinsic mechanical properties that, in turn, lead to changes in fracture resistance and overall bone matrix quality.

4:00 PM Y2.7/R2.7

Elastic Modulus of Dental Enamel: Effect of Enamel Prism Orientation and Mineral Content. Virginia Lea Ferguson[1,2], Alan Boyde[3] and Andy J. Bushby[2]; [1]Department of Aerospace Engineering, University of Colorado, Boulder, Colorado; [2]Department of Materials Science and Engineering, Queen Mary, University of London, London, United Kingdom; [3]School of Medicine and Dentistry, Queen Mary, University of London, London, United Kingdom.

Nanomechanical properties of mineralized tissues are determined by two main factors: microstructural tissue organization and relative composition of organic, mineral, and water phases. We combine nanoindentation and quantitative backscattered electron (qBSE) imaging to understand how these competing factors influence material properties at the ultrastructural and tissue level. Equine tooth enamel provides an ideal configuration to study the combined effects of enamel prism orientation and mineralization. Equine teeth undergo constant wear and growth thus necessitating longitudinally graded mineral content that increases with enamel maturity towards the biting surface. Hunter-Schreger bands (HSBs) extend from the dentino-enamel junction to the enamel surface in a direction perpendicular to the long axis of the tooth. Prisms within one band lie parallel to each other and at an angle to prisms in adjacent bands thus allowing investigation of crystallites in varying orientations. An equine (2-year-old) tooth, embedded in poly-methylmethacrylate, was sectioned longitudinally, polished, and carbon coated. qBSE images were collected to survey the tooth and for image analysis of prism geometry and mineralization level. Nanoindentation arrays measured elastic modulus in a 3.5 cm long array (500μm spacing) that extended from newly formed to fully mature enamel and in a tight array of indent sites (5μm spacing) over six partially mineralized HSBs. A relationship between the mineralization and modulus is presented which shows that elastic modulus increases dramatically as remaining pore spaces, located in regions of already highly mineralized enamel, are filled. In fully mature enamel, where modulus values exceed 80 GPa, prism orientation causes small perturbations (<1.5 GPa) in modulus values but remains a major contributor to enamel stiffness. Indentations spanning HSBs in immature, poorly mineralized enamel yield modulus values that vary with prism orientation in a sinusoidal-like pattern: transversely oriented prisms (11 GPa) are >2x stiffer than longitudinal prisms (4.5 GPa). We relate this to the packing of the mineral crystallites and organization of the pore spaces. In enamel, the high elastic modulus results largely from its sophisticated ultrastructural organization. Elucidating the ultrastructure of dental enamel will add both to our understanding of mineralized tissues and advance the development of novel biomimetic materials.

4:15 PM Y2.8/R2.8

Contribution of Collagen, Mineral, and Water Phases on Nanomechanical Properties of Bone. Amanpreet Kaur Bembey[1], Vanessa Koonjal[1], Virginia L. Ferguson[2], Andrew J. Bushby[1] and Alan Boyde[3]; [1]Department of Materials, Queen Mary University of London, London, United Kingdom; [2]BioServe Space Technologies, Engineering Centre, University of Colorado, Boulder, Colorado; [3]School of Medicine & Dentistry, Queen Mary University of London, London, United Kingdom.

Mechanical properties of bone are a consequence of the interaction between mineral, collagen and water. Mechanisms by which collagen orientation and mineral content influence mechanical properties of bone are poorly understood. Storage and preparation methods influence measurements of bone mechanical properties. Nanoindentation is a powerful method to examine mechanical properties of bone at the microstructural scale. Surface effects complicate nanoindentation of physiologically relevant bone samples. Thus, most studies examine dried, embedded, or included bone. To date, mechanical properties of mineral or collagen at the nano-scale are poorly defined. Beams of equine cortical bone were prepared to examine effects of dehydration and embedding and to study contribution of collagen and mineral to nano-scale material properties. Six beams were tested: untreated (hydrated); dehydrated in air, 100% ethanol; or embedded in poly-methylmethacrylate (PMMA) for one normal, one decalcified, and one deproteinated bone sample. Elastic modulus was obtained by nanoindentation using spherical indenters transverse and longitudinal to the bone axis. Dynamic mechanical analysis (DMA) data was obtained for same samples corresponding to longitudinal direction (AJ Bushby et al., JMR 2004). Statistical comparisons were performed using Student's t-test, α=0.05. Nanoindentation is normally relatively insensitive to anisotropy. Untreated bone did not demonstrate significant difference between two orientations. However, dehydration of bone in 100% ethanol emphasised anisotropy of the bone structure with mean elastic modulus increasing 37% from transverse to longitudinal direction. This anisotropy was reduced when subsequently embedded in PMMA. Influence of water on mechanical properties of bone is evident, but the manner in which liquid interacts with collagen and mineral is unclear. Deproteined sample showed more anisotropy than decalcified sample highlighting the importance of mineral crystal orientation. DMA and nanoindentation produced comparable results in the same orientation. Nanoindentation of bone in various conditions can reveal information about the ultrastructure of bone and role of the components including water.

4:30 PM Y2.9/R2.9

Nanoindentation of Bone in a Physiological Environment. Riaz Akhtar, Stuart Morse and Paul Mummery; School of Materials, University of Manchester, Manchester, Lancashire, United Kingdom.

Over the past decade nanoindentation has been established as an effective method to measure the mechanical properties of bone tissue at the nano scale. Although it is well documented that the mechanical properties of macroscopic bone specimens vary depending on whether the samples are tested dry or wet, nanoindentation is generally conducted on dehydrated bone tissue at room temperature, primarily because nanoindentation systems are extremely sensitive to changes in environmental conditions such as humidity and temperature. Other factors which tend to lead to spurious data when specimens are tested in liquid include surface roughness and swelling of cancellous bone, as well as small capillary forces acting on the indenter tip. In this study, these problems were overcome by using a specially constructed liquid cell with an extension piece that allowed the indenter tip to be submerged under 5 mm of liquid. A heating element with a temperature control unit was used to maintain testing temperature at 37°C. The liquid cell setup was calibrated using fused silica and single crystal [100] silicon. The mechanical properties of the calibration materials were found to be similar when tested in dry and in physiological conditions. The elastic modulus and hardness of cortical and cancellous specimens, of both bovine and human bone, were investigated by using the nanoindentation liquid cell under physiological conditions. During initial testing in distilled water it was found that a hydrated oxide layer formed on the surface of trabeculae. However, subsequent testing in simulated body fluid allowed trabeculae to be probed reliably. The elastic modulus and hardness of bone tissue were found to decrease when dry specimens were rehydrated and tested in physiological conditions. Despite higher thermal drift, reproducible data have been obtained. It is suggested that nanoindentation in physiological conditions gives a better estimate of the mechanical properties of bone *invivo* at the nano scale rather than nanoindentation under conventional conditions.

4:45 PM Y2.10/R2.10

Effect of Mineral Content on the Nanoindentation Properties and Nanoscale Deformation Mechanisms of Bovine Tibial Cortical Bone. Kuangshin Tai[1], Hang J. Qi[2] and Christine Ortiz[1]; [1]Materials Science and Engineering, Massachusetts Institute of Technology, Cambridge, Massachusetts; [2]Mechanical Engineering, Massachusetts Institute of Technology, Cambridge, Massachusetts.

Cortical bone is a complex, load-bearing, hierarchical biocomposite material whose fine details of nano- to microscale structural organization, heterogeneity, composition, and mechanical properties are known to have profound effects on the macroscopic mechanical function and dysfunction of the tissue. Mineral content is one critical parameter affecting mechanical performance that varies with age, disease, and injury. In this study, a combination of nanoindentation, tapping mode atomic force microscopy (TMAFM), scanning electron microscopy (SEM), low-vacuum back-scattered electron detection, and Raman spectroscopy were used in conjunction with finite element analysis (FEA) and continuum elastic contact mechanical theory to assess the nanoscale structure-mechanical property relationships as a function of mineral content. Samples were cut from between the tibial metaphysis and diaphysis region parallel to the bone long axis, polished to a 0.05 m finish, and progressively demineralized with phosphoric acid and ethylenediaminetetraacetic acid. Nanoindentation experiments were performed on hydrated samples using a Berkovich diamond indentor (end-radius, RTIP=180nm) perpendicular to the osteonal axis up to a maximum force of 1000μN and depth of 500nm (containing a maximum of 31 type I collagen fibrils within the contact area). A nonlinear increase in elastic modulus with increasing mineral content was observed ranging from 2GPa (0 wt%) to

7-12GPa (58 wt%). 3D elastic-perfectly plastic FEA numerical fits to the nanoindentation data resulted in a yield stress, Y, that increased with increasing mineral content from a 4 wt% mineral sample (Y 0.2 +/- 0.08GPa) that was 33% less than that of the undemineralized sample. The characteristic 67nm axial banding for type I collagen fibrils was observed in TMAFM and SEM images for all partially and fully demineralized bone specimens. High resolution TMAFM images after nanoindentation allowed the direct visualization of nanoscale mechanisms of deformation. For the samples with low mineral content (wt%), the collagen fibrils within the indent region retained their banding and the integrity of their interfaces while conforming to the probe tip geometry up until maximum loads of 1000μN. At higher maximum loads of 7000μN, the collagen banding was destroyed in a localized region at the probe tip apex, suggesting mechanical denaturation. The undemineralized sample shows flattening of topographical features and pileup along the edges of the indent region at maximum loads of 500μN possibly due to a pressure induced structural transition of the mineral component. FEA simulations of these experiments reveal that at a maximum load of 1000μN, the pressure ranges up to 520MPa, which is close to the pressure required for phase transition in sintered, synthetic dense HA. These different mechanisms are thought to contribute to an overall transformation toughening mechanism originating at the nanoscale level.

SESSION Y3/R3: Joint Poster Session: Nanomechanics & Tribology of Biological Materials
Chairs: David Bahr, Yang T. Chang, Adrian Mann and Kathryn Wahl
Monday Evening, November 29, 2004
8:00 PM
Exhibition Hall D (Hynes)

Y3.1/R3.1

Impedance Spectroscopy and Nanoindentation of Fuzzy Conducting Polymer Films on Neural Prosthetic Devices. Junyan Yang[1], David Martin[1] and David Martin; [1]University of Michigan, Ann Arbor, Michigan; [2], University of Michigan, Ann Abror, Michigan.

Microfabricated electrodes are being actively developed for the direct communication with neurons. We have been investigating the use of conducting polymer films for improving the long-term performance of these devices. By correlating measurements of probe electrical properties with surface morphology we have found that maximizing the effective surface area of the electrode coating makes it possible to minimize the electrical impedance. Nanoindentation allows for precise measurements of the mechanical properties of the thin polymer films as a function of their morphology and thickness. The micromechanisms of plastic deformation can be evaluated by correlating the indentation response with microstructural studies of the polymer before and after deformation. In this report, the electrical and mechanical properties of thin, fuzzy conducting polymer coatings on the neural prosthetic devices have been characterized by using impedance spectroscopy and nanoindentation. We found that the effective stiffness and electrical properties of the conducting polymer films varies with thickness and morphology. Our results reveal that for conducting polymers PPy and PEDOT the minimum impedance correlates well with the mechanical properties. In this series of materials, the films first become softer and rougher and then stiffen and get more dense as the polymerization continues. The lowest impedance films are also those that have the softest, most compliant mechanical response. This is consistent with the interpretation that the high surface area of the films promotes the most facile charge transport. This information provides clues for improving the long-term performance of these electrodes in-vivo.

Y3.2/R3.2

Aromatic Thiols and Plant Sterol Derivatives as Friction Modifiers. M. Ruths[1], S. Lundgren[1,2], K. Boschkova[1] and K. Persson[1]; [1]YKI, Institute for Surface Chemistry, Stockholm, Sweden; [2]Dept. of Chemistry, Surface Chemistry, Royal Institute of Technology, Stockholm, Sweden.

Aromatic molecules are less flexible than alkanes and have more complex intermolecular interactions, which makes their lubricating properties interesting both from a fundamental and from a practical point of view. Friction force microscopy (FFM) and the surface forces apparatus technique (SFA) were used to study the boundary friction of single- and multicomponent self-assembled monolayers of aromatic thiols and silanes, plant sterol derivatives, and rosin acids. At conditions of low adhesion, good agreement was found between friction coefficients measured with the two techniques despite the large differences in the contact areas, forces and pressures. In mixed aromatic thiol monolayers, friction coefficients and transition pressures are intermediate to the ones found in monolayers of pure compounds, suggesting a way to tune the friction response by varying the composition.

Y3.3/R3.3

Effect of Flour on Mechanical Properties of Teeth Demineralized by Use of Othodontic Appliances. Claudia Centeno[2], Ulises Ruiz[2], Oscar Contreras[1] and Enrique C. Samano[1]; [1]CCMC-UNAM, San Ysidro, California; [2]Facultad de Odontologia, UAEM, Toluca, Mexico.

The risk of dental caries increases with the use of orthodontic appliances, and it does not only depend on patients's oral hygiene. Caries causes that the enamel of teeth demineralizes close to the orhodontic bracket. The hardness of teeth consequently decreases, becoming brittle and loose. The type of adhesive used to fix orthodontic brackets might reduce or not enamel demineralization. Previous studies have shown that a resin-modified glass ionomer (RMGI) cement and fluoride varnish might inhibit demineralization. The purpose of this work is to evaluate the effect of a fluoride-releasing cavity varnish on mechanical properties of dentin and enamel in regions adjacent to orthodontic brackets bonded with RMGI and composite resin cements. The demineralization effect on teeth was assesed by measuring hardness and relative elastic modulus on dental pulp, dentin and enamel around the bracket area by nanoindentation methods. Nanoindentation was performed using a TriboScope from Hysitron. For this purpose two sets of samples were prepared: one set with no orthodontic treatment and the other one with orthodontic treatment using the adhesive already described. A relationship between mechanical properties and fluor content is found. The amount of fluor in the teeth was obtained by X-ray photoelectron Spectroscopy (XPS). The morphology of the samples is determined in situ by means of the TriboScope in the imaging mode.

Y3.4/R3.4

Variation of Ultrastructure and Nanomechanical Properties of Individual Chondrocytes with an Increasingly Thick Pericellular Matrix. Laurel J. Ng[1], Alan Grodzinsky[1,2,3] and Christine Ortiz[4]; [1]Biological Engineering, MIT, Cambridge, California; [2]Electrical Engineering and Computer Science, MIT, Cambridge, Massachusetts; [3]Mechanical Engineering, MIT, Cambridge, Massachusetts; [4]Material Science and Engineering, MIT, Cambridge, Massachusetts.

Chondrocytes make up <10% of cartilage volume and are solely responsible for the synthesis, assembly, and catabolism of the extracellular matrix (ECM) molecules. A mechanical property gradient exists from the cell (elastic modulus, E 1kPa) to its surrounding pericellular matrix (PCM, E 60kPa) to the bulk ECM (E 1MPa), which acts to regulate the amount of cell deformation caused by external loads applied to the tissue. The PCM, in particular, plays a role in the both biomechanical and biochemical cellular function, modulating the strains felt on the cell during compression and controlling the immediate environment surrounding the cell. Our objectives in this study were (1) to directly visualize the in vitro synthesis of ECM macromolecules from individual chondrocytes and the evolving ultrastructure of the PCM via tapping mode atomic force microscopy (TMAFM) imaging and (2) to correlate the production of ECM by individual chondrocytes with changes in the nanomechanical properties of the cell-PCM composite via nanoindentation, both as a function of time in culture. To address the first goal, chondrocytes isolated from bovine articular cartilage were cultured and released from 3mm diameter alginate beads at intervals over one month, deposited onto freshly cleaved mica, and visualized using TMAFM in ambient conditions. At day 4 of the culture, individual collagen fibrils were observed emanating from the cell surface (88$\pm$9nm diameter, 58$\pm$6nm characteristic banding periodicity). At day 6 of the culture, a distinct halo of PCM (thickness 9μm) was present and by day 18, a dense, homogeneous, network of collagen fibrils was clearly visibly. For the second objective, culture-released cells were deposited onto silicon plates containing pyramidal 20μm diameter wells, each of which held individual live chondrocytes in place for both TMAFM and single cell nanoindentation experiments in fluid as a function of culture time. This method also allows for visual confirmation of chondrocyte phenotype and size measurement (and therefore PCM growth) of each cell that is being studied. Nanoindentation using Si3N4 pyramidal probe tips (radius 50nm) showed a distinct increase in compressive stiffness with culture time due to the growing PCM, as reflected by an increase in the slope of the force vs. indentation depth curves. The indentation data exhibited nonlinear hysteretic behavior, indicating the cell and its PCM are viscoelastic or perhaps poroelastic. Due to the small probe tip end radius, contact is likely made with individual molecular components of the PCM (e.g., proteoglycans and collagen fibrils) and not representative of bulk PCM properties. To measure the larger scale material properties of the PCM, further nanoindentation experiments are currently underway using μm-sized colloidal tips. Finite element modeling is being used to interpret this data and predict nanomechanical properties such as elastic and viscoelastic properties such as storage and loss moduli.

Y3.5/R3.5

Effects of Osteopontin on Nanomechanics and Microstructure of Mouse Bones. Beril Kavukcuoglu[1], Courtney West[3], David Denhardt[2] and Adrian Mann[1,3]; [1]Ceramic and Materials Engineering, Rutgers University, Piscataway, New Jersey; [2]Cell Biology and Neuroscience, Rutgers University, Piscataway, New Jersey; [3]Biomedical Engineering, Rutgers University, Piscataway, New Jersey.

Osteopontin (OPN), a phosphorylated glycoprotein, is among the most abundant non-collageneous bone matrix proteins produced by osteoblasts and osteoclasts. OPN has been implicated in bone formation, resorption and remodeling, however, previous studies have presented contradictory results regarding the effect of OPN on the mechanics and microstructure of bone. This study has used nanoindentation to identify local variations in elastic modulus and hardness of osteopontin deficient (OPN -/-) and wildtype control (OPN+/+) mouse bones. Specifically, the study has looked at changes in the bones mechanical properties with the mouse age, background and sex. The mechanical properties have been correlated with changes in the local structure of the bone as observed with SEM, FTIR , XRD and micro-Raman. Cortical sections of femurs from 3 week old and 6 month old mouse bone were tested and compared. The results suggest that there are large, abrupt variations in mechanical properties across the femur radial section for 3 week old mouse bone. The hardness (H) drops down significantly towards the inner and outer sections resulting in a standard deviation of 2.6 GPa with a mean H=5.1 GPa. In order to obtain statistically comparable data only the hardness measurements taken from interior area, which show a standard deviation of 1.7 GPa with mean H=6.5 GPa are taken into consideration. The hardness of the 6 month old mouse bone has a standard deviation of 0.25 GPa and a mean H=1.4 GPa. The hardness along the radial axis of the 6 month old was found to be quite homogeneous. Just like hardness, elastic modulus also shows abrupt variations along the radial axis of the young mouse bone whereas it remains quite constant for the 6 month old. Therefore we conclude that the mechanical properties of the mouse bones decrease substantially with maturity, but statistically hardness and elastic modulus are more homogeneous in mature bones than young ones. We found a similar variation in both OPN-/- and OPN+/+ bones, but the magnitude of the mechanical variation appears to depend not only on the age, but also the presence or absence of OPN. The mechanical variations correlate with changes in the degree of mineralization and crystallinity of the bone as revealed by the structural analysis. That is, high mineral content and high crystallinity corresponds to regions of increased hardness and stiffness. The results for OPN-/- and OPN+/+ mouse bones are particularly important as control of OPN activity has been postulated as a potential treatment for bone pathologies that exhibit a change in the bone mineralization, such as osteoporosis, osteopetrosis and Paget's disease. Understanding the effects of OPN on bone mechanics is a vital step in the development of these new treatments.

Y3.6/R3.6

Spatially Dependent Mechanical Properties of Rat Whiskers for Tactile Sensing. Elizabeth K. Herzog[2,1], David F. Bahr[1], Cecilia D. Richards[1], Robert F. Richards[1] and David M. Rector[3]; [1]Mechanical and Materials Engineering, Washington State University, Pullman, Washington; [2]Materials Engineering, Purdue University, West Lafayette, Indiana; [3]Veterinary and Comparative Anatomy, Pharmacology, and Physiology, Washington State University, Pullman, Washington.

A new generation of sensors based on biologically inspired whisking action will help determine the presence and location of solid objects and fluid vortices similar to mechanisms used by whisker bearing animals such as rats and seals. A key to this system is the mechanical response of the whiskers to applied forces, which will be impacted by the elastic properties of these biologically inspired structures. To determine the effectiveness of biological whisking structures the elastic, viscoelastic, and plastic properties of whiskers from laboratory rats were determined. By using dynamic nanoindentation, we demonstrate that mechanical properties are essentially uniform by cross section over an entire whisker, but vary longitudinally from the whisker base (a 3.9 GPa elastic modulus) to the tip (a 3.1 GPa elastic modulus). Several recent studies show propagation of high frequency information through whiskers that are tuned by their physical properties, and have measured an average elastic response of approximately 3.5 GPa. In order to fully understand and model these properties, this study demonstrates the need for a more complex whisker structure than previously assumed.

Y3.7/R3.7

Nano-mechanical Testing of a Biological Protective Coating of a Visco-elastic Material. Niels Holten-Andersen[1], Nelle Slack[2], Frank Zok[3] and Herbert Waite[1]; [1]BMSE, UCSB, Santa Barbara, California; [2]Veeco Metrology, LLC, Santa Barbara, California; [3]Materials, UCSB, Santa Barbara, California.

The holdfast structure of mussels, the byssus, is a structure with unique visco-elastic mechanical properties evolved to withstand the challenges of the turbulent saline environment of the intertidal zone. Each byssal thread consists of three functional domains: the glue in the plaques which bonds the thread to a variety of hard surfaces, the fibrous collagenous core which connects with the glue and resists the applied loads of waves, and, the topic of this investigation, the coating covering all parts of the byssus. The major protein of the coating is Mussel foot protein-1 (Mfp-1). A large database in biochemistry, surface chemistry, molecular biology and covalent modification exists on Mfp-1 and it has traditionally been considered the best known of the mussel adhesive proteins. Mfp-1 is the active ingredient in a broad spectrum cell and tissue attachment factor and analogs have been used to anchor tethered pegylated polymers to implant surfaces thereby successfully establishing nonfouling implant surfaces in cell culture. However, ironically Mfp-1 is not the adhesive but rather the coating of the mussel byssus. In the distal portion of the thread the coating has a micron-sized knob-like consistency. This is the part of the thread outside the mussel shell and hence we speculated that it endows the threads with protection against abrasion. The mechanical properties of the coating have been investigated with the use of nano-indentation and the coat was found to confer mechanical protection of the thread interior due to a significantly higher hardness. Our data furthermore indicate that the thread distal coating is a metal-protein composite. The proteinaceous matrix of the distal coat additionally contains the elements Fe, Si, Al and Br. However, the relative distribution and specific form of these elements in the coat are currently unknown. Their potential correlation with the knob-like structure of the distal coat and their role in the coats mechanical behavior is intriguing and has been further investigated. Finally despite its apparent hardness, the distal coating accommodates strains of up to 70%. Current data indicate that the distal coat rearranges without loss of integrity in accordance with the tension experienced by a thread. A fundamental understanding of how the molecular structure and function are adaptively related in the mussel byssus coating would therefore greatly assist and accelerate the intelligent design of unique bio-inspired coatings which are durable, protective and extensible.

SESSION Y4: Mechanical Properties of Bio-Inspired and Biological Materials II
Chairs: Christian Hellmich and Franz Ulm
Tuesday Morning, November 30, 2004
Room 205 (Hynes)

8:30 AM *Y4.1

Computational Mechanics Routes to Explore the Origin of Mechanical Properties in a Biological Nanocomposite: Nacre. Dinesh R. Katti and Kalpana S. Katti; Civil Engineering, North Dakota State University, Fargo, North Dakota.

Nacre, the iridescent inner layer of seashells is a well characterized biological nanocomposite exhibiting exceptional mechanical properties. Nacre is a laminated nanocomposite consisting of micron sized pseudohexagonal aragonitic calcium carbonate platelets with about 20 nanometer thick organic layer sandwiched between the platelets. Although, nacre is composed of 95 to 98 % calcium carbonate, the fracture toughness of nacre is reported to be several orders of magnitude higher than that of aragonite. This nanocomposite has been studied extensively as a model system for the design of new biomimetic nanocomposites. The nano and micro architecture of nacre has many features and nuances, which have been attributed as possible reasons for the exceptional mechanical properties. However, nacre being a biological material, the existence of some of these nuances may be purely for biological reasons and may have very little contribution to the mechanical properties. In our work, we have used computational mechanics routes to model and simulate observed macro response to quantitatively evaluate the contribution of various components of the nano and micro architecture of nacre on the mechanical properties. Specifically, our work sheds light on the components and features of the nacre architecture affecting the elastic response, the yield stress and toughness.

9:00 AM Y4.2

Lessons for New Classes of Inorganic/Organic Composites from the Spicules and Skeleton of the Sea Sponge Euplectella By R. Trejo1, E. Lara-Curzio1, M. Rodriguez2, K.Tran2, and G. Mayer2. George Mayer[1], Rosa Trejo[2], Edgar Lara-Curzio[2], Maria Rodriguez[1] and Ken Tran[1]; [1]Materials Science & Engineering, U. of

Washington, Seattle, Washington; [2]Mechanical Testing Dept., Oak Ridge National Lab, Oak Ridge, Tennessee.

Studies have been carried out on the structures and mechanical characteristics of an unusual family of sea sponges under the classification of Hexactinellida, subclass Euplectella. The sponge spicules have been of interest to materials scientists because of their potentially important optical, coupled with mechanical, properties. The structures of the species Hexactinellida are characterized by a concentric ring appearance in the cross-section, which is a composite of hydrated silica, coupled with silicatein as a thin layer at the ring interfaces. The mechanical behavior and the toughness of the spicules have been examined with the aid of a special fiber testing method, coupled with SEM observations. It appears that there may be common mechanisms underlying toughness in rigid natural composites with high ratios of mineral/organic phase. In addition, novel pressurization tests of a portion of the sponge skeleton have provided information about the resilience of the skeleton, which resembles a self-supporting glass winding of a cylindrical composite structure. 1- Oak Ridge National Laboratory, Oak Ridge, TN 2- University of Washington, Seattle, WA

9:15 AM Y4.3
Structure/Property Relationships of Seashells.
David James Scurr and Stephen James Eichhorn; Materials Science Centre, UMIST, Manchester, United Kingdom.

This study characterises the razor shell, *Ensissiliqua*, using scanning electron microscopy (SEM), x-ray diffraction, nanoindentation, microhardness, and Raman spectroscopy. It has been shown that the shell is composed almost entirely of calcium carbonate ($CaCO_3$) >95%, in the aragonite polymorph, where the upper and lower regions of the shell have a microstructure of simple and complex crossed lamellar layers respectively. These layers are interspersed by prismatic layers of a completely different crystallographic orientation. Nanoindentation and microhardness have shown that the structure is anisotropic, and Raman band shifts have been observed within these indented/deformed areas of shell. Raman band shifts have also been observed during hydrostatic pressurisation of powdered shell up to 7 GPa, at a shift rate of 3.9 cm^{-1}/GPa. The use of energy variable synchrotron x-ray diffraction has shown that the calcium carbonate crystals of the shell are preferentially orientated as a function of depth. Residual stresses, and changes in crystallographic orientation of the prismatic layer have also been observed using this technique. These features are thought to contribute to the fracture toughness of the shell by preventing crack propagation through the microstructure, by arresting cracks and by causing delamination. The presence of prismatic layers and elevated residual stresses in these areas leads to the delaminating of shell sections rather than catastrophic failure through the entire structure. This study provides insight into the relationship between microstructure and mechanical properties of the shell, and could ultimately aid biomimicry.

9:30 AM Y4.4
Effects of Wetting and Desiccation on the Creep Properties of Natural Silk. Joanne Ritchie[2], Christopher Smith[2], Fraser I. Bell[2], Iain J. McEwen[2] and Christopher Viney[1,2]; [1]School of Engineering, University of California at Merced, Merced, California; [2]Chemistry, School of Engineering and Physical Sciences, Heriot-Watt University, Edinburgh, Midlothian, United Kingdom.

Spider and silkworm silks have been studied extensively during the past two decades, prompted by the high mean values of breaking strength, initial stiffness, and toughness reported for some of these materials. It is necessary to recognize, however, that the impressive tensile properties are deduced from experiments that reflect neither the natural in-service loading conditions, nor the likely loading conditions that would pertain to many of the proposed uses of biomimetic analogues of natural silk. Tensile testing is routinely performed at constant strain rate, on a timescale where the test is completed (the sample breaks) before the contribution of viscoelastic phenomena such as creep and stress relaxation can be properly assessed. We have devised a simple method for quantifying the creep resistance of silk fibres–in other words the ability of silk to maintain dimensional stability while supporting a constant load. We demonstrated (C. Smith, J. Ritchie, F.I. Bell, I.J. McEwen and C. Viney, *JournalofArachnology* 31:421-424, 2003) that there is a limiting creep stress: if samples are loaded smoothly and quickly to a constant stress lying above the limiting creep stress, they break within a few seconds of the stress being applied. The magnitude of the limiting creep stress is equal to approximately one fifth of the fracture stress recorded in conventional constant strain rate tests. We also demonstrated that creep is significant at stresses that are small compared to the conventional yield strength. Here we extend the study of creep to investigate the effects of immersion in water and in ethanol. Experiments are conducted by attaching a small weight (an appropriate number of office staples) to an approximately 20 cm length of silk (major ampullate–dragline–silk from *Nephilaclavipes* spiders, and cocoon silk from *Bombyxmori* silkworms) and monitoring extension as a function of time while the samples are suspended vertically in the liquid environment. Samples are previously conditioned by immersing the unconstrained fibres in the liquid, to allow them to supercontract or relax if the liquid promotes such a response. Allowance for buoyancy is made when calculating the net force applied to samples by the weight of the staples. Water is found to have a plasticizing effect on both types of silk, significantly exacerbating the rate of creep in response to a given load, and significantly shortening the creep life of the silk. Ethanol, in contrast, acts as a desiccant, significantly decreasing creep rates and increasing creep lifetimes. These results draw attention to an important limitation that must be overcome if biomimetic silk is to be used in applications where dimensional stability is required while large loads are being supported for long times, especially in a humid environment. The results also point to the molecular origins of the creep sensitivity, and thus to ways of making silk and silk analogues less susceptible to creep.

10:15 AM *Y4.5
Micromechanics-Based Modeling of Biological Tissues Using the High-Fidelity Generalized Method of Cells.
Marek-Jerzy Pindera, Civil Engineering, University of Virginia, Charlottesville, Virginia.

The High-Fidelity Generalized Method of Cells is a semi-analytical micromechanics model developed for periodic multiphase materials with locally arbitrary microstructures [1,2]. The model's analytical framework is based on the homogenization technique for periodic media, but the method of solution for the local displacement and stress fields borrows concepts previously employed in constructing the Higher-Order Theory for Functionally Graded Materials [3], in contrast with the homogenization technique. The approach produces a closed-form macroscopic constitutive equation valid for both uniaxial and multiaxial loading. The recent extension of the model incorporates finite deformation and quasi-linear viscoelasticity capabilities to enable modeling of heterogeneous materials such as fiber-reinforced rubbers or certain types of biological tissues [4,5]. The model's ability to accurately estimate both the homogenized nonlinear response and the local stress fields at the phase level has been demonstrated by comparison with exact elasticity and finite-element approaches. In the present communication, we employ the extended micromechanics model to predict the response of two different types of mital valve chordae tendineae with two characteristically different microstructures for which some limited experimental data is available. In particular, the response of repeating unit cells characterized by wavy collagen fibrils is compared with experimental response of chordae tendineae possessing different collagen fibril crimp periods under constant strain rate, creep and relaxation loading. This comparison clearly demonstrates the ability of the extended micromechanics model to explain the experimentally-observed differences in the large-deformation responses rooted in the different microstructural details of the different chordea tendineae types, while also suggesting how the model can be used to determine the fundamental data on the response of the in-situ-constituents. 1. Aboudi, J., Pindera, M-J., and Arnold, S.M., "Linear Thermoelastic Higher-Order Theory for Periodic Multiphase Materials," ASME J. Applied Mechanics, Vol. 68, No.5, 2001, pp. 697-707. 2. Aboudi, J., Pindera, M-J., and Arnold, S.M., "Higher-order Theory for Periodic Multiphase Materials with Inelastic Phases," In. J. Plasticity, Vol. 19, 2003, pp. 805-847. 3. Aboudi, J., Pindera, M-J., and Arnold, S.M., "Higher-Order Theory for Functionally Graded Materials," Composites: Part B, Vol. 30B, No. 8, 1999, pp. 777-832. 4. Aboudi, J. and Pindera, M-J., "High-Fidelity Micromechanical Modeling of Continuously Reinforced Elastic Multiphase Materials Undergoing Finite Deformation," Mathematics and Mechanics of Solids (in press). 5. Pindera, M-J. and Aboudi, J., "High-Fidelity Micromechanical Modeling of Viscoelastic Multiphase Materials Undergoing Finite Deformations: User's Guide and Model Validation," EMC Report No. 2003-02, Engineered Materials Concepts, LLC, Charlottesville, Virginia.

10:45 AM Y4.6
Characterization of Semiflexible Fibril Networks Formed Via Intramolecular Folding and Self-Assembly of Amphiphilic β-Hairpin Molecules. Bulent Ozbas[1,3], Karthikan Rajagopal[2], Juliana Kretsinger[2], Joel P. Schneider[2] and Darrin J. Pochan[1,3]; [1]Materials Science and Engineering, University of Delaware, Newark, Delaware; [2]Department of Chemistry and Biochemistry, University of Delaware, Newark, Delaware; [3]Delaware Biotechnology Institute, University of Delaware, Newark.

We present the formation of hydrogels via the intramolecular folding and consequent self-assembly of 20 amino acid long β-Hairpin peptide molecules. The peptide molecules are locally amphiphilic with two linear strands of alternating hydrophobic valine and hydrophilic lysine amino acids connected with a D-Proline-L-Proline-Threonine turn sequence. At pH 7.4 and low ionic strength solution conditions, dilute (? 2 wt.%), homogeneous solutions of peptide exhibit the viscosity of pure water. Circular dichroism spectroscopy shows that at pH 7.4 molecules are unfolded in the absence of salt. By raising the ionic strength of the solution the electrostatic interactions between charged lysines are screened and the peptide arms are forced into a parallel β-sheet secondary structure by the turn sequence. These folded molecules intermolecularly assemble via hydrophobic collapse and hydrogen bonding into a three dimensional network. Rheological measurements demonstrate that the resultant supramolecular structure forms an elastic material, whose structure, and thus modulus, can be tuned by salt concentration and temperature. TEM, SANS, and rheological data reveal that the elasticity arises from a network consisting of semi-flexible fibrillar assemblies, micrometers in length and nanometers in width, with permanent junction points. The experimental results are compared with scaling relationships developed within semiflexible network theories.

11:00 AM Y4.7
Nanoscale Origins of Spider Dragline Mechanical Properties.
Jessika E. Trancik[2,3], Jan T. Czernuszka[2], Fraser I. Bell[4] and Christopher Viney[1,2,4]; [1]School of Engineering, University of California at Merced, Merced, California; [2]Department of Materials, University of Oxford, Oxford, United Kingdom; [3]Earth Institute, Columbia University, New York, New York; [4]Chemistry, School of Engineering and Physical Sciences, Heriot-Watt University, Edinburgh, Midlothian, United Kingdom.

Transmission electron microscopy (electron diffraction), supported by x-ray diffraction, was used to characterize the amount and size distribution of ordered regions in the dragline silk of black widow spiders *Latrodectushesperus*. A bimodal size distribution of ordered regions was deduced; results indicated one population of crystals having a mean size of 2 nm, and another that spans the size range 40-120 nm. Tensile properties of the dragline, including the axial modulus, were measured under conditions of controlled temperature and humidity. Several mechanical models of silk, in which the material is treated as a composite of crystalline and amorphous and/or interphase material, were used to predict the tensile modulus of the dragline along the fibre direction, for comparison with the measured mean value. The models considered include the Voigt average (which assumes that the fibres/crystals are continuous, and that the strain is the same in all components of the composite), a modified Halpin-Tsai model (which is suitable for predicting the longitudinal elastic modulus for short aligned fibre composites, and thus is more appropriate for silk), and the shear-lag or Cox model (which is a modification of the Voigt average that takes into account a discontinuous nature of stiff fibres/crystals and the resulting shear stress in the amorphous matrix; the shear stress arises because the stiff crystals restrain the deformation of the matrix, and is a maximum at the ends of the crystals). All the models yielded close approximations of the experimental elastic modulus of *L.hesperus* dragline, given realistic inputs for the moduli of the individual components and the percent crystallinity. A literature model for the stress-strain behaviour of silk (Y. Termonia, *Macromolecules* 1994, v.27, pp.7378-7381) was considered in the context of our experimental results for *L.hesperus* dragline. The average elastic modulus measured from *L.hesperus* dragline is 23 GPa - close to the 25 GPa theoretical modulus for the case of large crystals in Termonia's model. The tensile strength of *L.hesperus* dragline is ca. 1.7 GPa, close to the case predicted for small crystals in Termonia's model. Thus, a combination of the small and large crystals - as detected in our TEM studies - could explain the forced elongation behavior of *L.hesperus* dragline. Termonia's model assumes no breaking of crystallites. However, the larger crystals detected in *L.hesperus* dragline were found to be imperfect, as evidenced by lattice strains. Furthermore, their degree of orientation with respect to the fibre axis is less than that of the small crystals. These two factors mean that the larger, imperfect crystals may be able to deform plastically. Larger crystals could lead to a high elastic modulus without acting as stress centres past the yield point and thus, the plastic deformation of the fibre could be approximated by Termonia's stress-strain curve for the case of small crystals.

11:15 AM Y4.8
Shrinkage of Type I Collagen Molecules. Sidney Lees, Bioengineering, The Forsyth Institute, Boston, Massachusetts.

Bone and other mineralized tissues shrink when dried. Shrinkage defined as S = WT - DT/WT (1) Where WT = Wet Thickness and DT = Dry Thickness is not uniform in all orientations. Shrinkage measured along the axis of the bone shows no regularity. Radial shrinkage exhibits a highly linear dependence on the inverse wet density, as given by (2). S = 0.258X - 0.097 (2) Where X = $1/\rho$ and ρ = Tissue wet density This is similar to the linear dependence of the volume fraction of water on inverse wet density (3), except the slope for the shrinkage is 1/3 that for volume fraction. vf = 0.85X - 0.32 (3) Where vf = volume fraction of water This is not surprising since only a fraction of the tissue water lies between the collagen molecules. Pineri(1) et al. showed five regimes of water in the collagen structure, two intramolecular, two intermolecular. The fifth regime is free water. Most of the water is in the collagen structure, organized into various levels of crosslinking and interlinking. The volume fraction of water lost on drying corresponds to the loss of water between collagen molecules, as observed on a nanometer scale. On the other hand shrinkage represents macroscopic effects on the order of millimeters. Consider a section of compact bone perpendicular to the axis. The shrinkage at every point is the same. This indicates an orderly distribution of water in the wet tissue in the radial orientation. It has been previously shown that the lateral spacing between collagen molecules is linearly dependant on the inverse wet density (2). One line with positive slope was found for wet tissues and a different line with negative slope was found for dry tissues. The orderly condition indicated is associated with the lateral spacing of the collagen molecule, whereas there is no orderly condition in the axial orientation. The volume fraction of water is also related to the lateral distribution of the collagen. Since there is a close relationship between changes in water volume fraction and shrinkage, shrinkage pattern is controlled by the structure of the collagen. (1)Pineri, M., Escoubes, M., Roche, O. 1978. Biopolymers. 17.2799-815. (2)Lees, S. 2003. Biophysics Journal. Volume 85 204-207. (3)The equations are derived from unpublished data spanning a large range of density.

SESSION Y5: Mechanical Properties of Bio-Inspired and Biological Materials III
Chairs: Kalpana Katti and Franz Ulm
Tuesday Afternoon, November 30, 2004
Room 205 (Hynes)

1:30 PM *Y5.1
Fiber Networks and Applications to Tissue Scaffolds.
Eveline Baesu and Minrong Zheng; Engineering Mechanics, University of Nebraska-Lincoln, Lincoln, Nebraska.

Finite elastic-plastic deformation of a 2-D and 3-D fiber continuum is described such that the properties of the continuum can be inferred from those of each fiber family. The only constitutive input required by the theory is the one-dimensional elastic-plstic response of materials under simple tension. Sufficient conditions are given for the existence of an exact dual extremum principle used to prove uniqueness of solution. Applications of this model to the modeling bio-mimetic materials, especially tissue scaffolds, is emphasized. Interaction between cells and fibers is modeled by accounting for the adhesion forces. As discussion of the role of this interaction in the development of cells is included.

2:00 PM Y5.2
The Mechanical Behaviour of Healthy and Scarred Skin. Ben Russell[1], Abdul Sattar[2], Steve Eichhorn[1], Mark Ferguson[2] and Paul Mummery[1]; [1]School of Materials, University of Manchester, Manchester, United Kingdom; [2]School of Biological Sciences, University of Manchester, Manchester, United Kingdom.

Skin is a highly complex composite material that fulfils a multitude of functions whilst being able to operate under a wide variety of conditions. However, scar tissue can cause significant loss of function in addition to aesthetic complications. Treatments are being developed to mediate the effects of scarring. However, it is difficult to measure quantitatively the effects of these treatments and comparison is often made by simple visual inspection alone. The principal objective of this project is to investigate the architecture of the regenerated tissue (scar) and the effect this has on the mechanical properties of the scar and surrounding regions of skin. This may provide a route to developing such a quantitative technique. The layer of skin of most interest in this study is the dermal layer, as this is the major structural component of the skin. The properties of normal skin need therefore to be characterised, and related to the structure of the dermis. A brown rat animal model, rattus norvegicus, was used in the study. Scars of 10 mm length were made with a scalpel on the back of the rats and left for 21 days to heal. Some scars were treated with scar mediating drugs. Scarred and normal tissue specimens were removed from the rats and the mechanical properties evaluated using DMTA (Dynamic Mechanical Thermal Analysis), to characterise the viscoelastic response, and standard tensile testing. The results showed that the specimens containing the scarred tissue were stiffer, but less ductile, than the unscarred specimens. The effect of the mediating treatments was to make the scars behave more like the unscarred material. These data were used as constitutive relations within a numerical finite element model (FEM). The FEM was used to predict the stress/strain behaviour of skin/scar tissue and the effect of geometry, loading and property variation on the mechanical behaviour. Image correlation, where successive images of a specimen on straining are compared to monitor the full-field displacement, was

used to map the strains around scars. This was used to validate the FEM. Good agreement was found between the image correlation results and the predictions of the model. Raman spectroscopy was used to investigate the morphology of the collagen fibres in all tissue types. The treated scars had a more random collagen arrangement whilst the collagen in the untreated scars was more highly aligned. Histology on the treated and untreated scars confirmed these differences in the collagen morphology.

2:15 PM Y5.3
Uniaxial and Biaxial Mechanical Behavior of Human Amnion.
Michelle L. Oyen[1], Triantafyllos Stylianopoulos[1], Victor H. Barocas[1], Robert F. Cook[1] and Steven E. Calvin[1,2]; [1]University of Minnesota, Minneapolis, Minnesota; [2]Minnesota Perinatal Physicians/Allina Health System, Minneapolis, Minnesota.

Chorioamnion the membrane surrounding a fetus during gestation (the "amniotic sac") is a structural soft tissue for which the mechanical behavior is poorly understood despite its critical role in maintaining a successful pregnancy and delivery. Preterm rupture of the chorioamnion accounts for one third of all premature births. The structural component of chorioamnion is the approximately 50-100 micrometer thick amnion sublayer, which provides the membrane's mechanical integrity via a dense collagen network. Amnion uniaxial and planar biaxial tension testing was performed using monotonic loading, cyclic loading, and stress-relaxation. The prefailure material response is highly nonlinear, exhibiting an approximately quadratic response. Cyclic testing, both uniaxial and equi-biaxial, exhibited dramatic energy dissipation in the first cycle and an eventual stable hysteresis response with approximately 20% energy dissipation per cycle. Stress-relaxation testing, both uniaxial and biaxial, demonstrated a load dependent response and continued relaxation after long hold times. A nonlinear viscoelastic (separable) hereditary integral approach was used to model the amnion stress-strain-time response during relaxation. The mechanical results are discussed within the context of the in vivo clinical performance of amnion, including the potential for membrane repair.

2:30 PM Y5.4
Measurement of the Forces Exerted by Cells with Optimized Digital Image Speckle Correlation and FEA+. E. Guan[1], Sravanesh Muralidhar[2], Yajie Liu[3], Kaustabh Ghosh[2], Miriam Rafailovich[1] and Richard Clark[3]; [1]Materials Science and Engineering, State University of New York, Stony Brook, Stony Brook, New York; [2]Biomedical Engineering, State University of New York, Stony Brook, Stony Brook, New York; [3]Mechanical Engineering, State University of New York, Stony Brook, Stony Brook, New York.

Evidence has shown that mechanical force plays an important role in regulating the behavior of single cell and their communities. The force is mostly generated by the actin cytoskeleton and transmitted to the extracellular matrix (ECM) through cell-matrix adhesions. We have observed that the cytoskeleton can sense the mechanical rigidity of the substrate and able to rearrange its organization accordingly, attempting to match cell modulus, as closely as possible, to that of the substrate. We postulate that the driving force for this phenomenon is the minimization of the mechanical work exerted at the contact line by the cell. It is therefore important to be able to measure both the modulus of the cell as well as the traction forces exerted by cells. Traction force can be mapped from the deformation of the substrate exerted by cell. Based on Fredholm convolution, people have introduced various approaches to calculate forces. It's known that the accuracy of this inverse ill-posed method strongly depends on the precision of displacement measurement, which hasn't been studied well. The pre-knowledge on the cell boundary and the location of forces is also necessary. Fluorescent transfection is usually essential to locate cells and the forces. In this study, we introduced a novel approach to measure the traction force. The technique of Digital Image Speckle Correlation (DISC) was optimized for the measurement of the deformation generated by cells on the cross-linked hyaluronic acid gel to produce the best spatial resolution and the highest precision. It analyzes two images taken with a confocal microscope before and after the substrate is deformed, and yields a displacement field of the substrate surface through the tracking of speckles, the geometric features such as black and white spots in the images. Fluorescent beads were embedded into the HA gel before cross-linking to form high-density speckle pattern for DISC to analyze. Calibration shows that the accuracy of the displacement in our experiment can be as high as 0.03 microns with a 63X objective lens. The viscosity of the HA gel was determined by rheology tests. Knowing the modulus of HA substrate, the traction force was then computed simply by the application of Finite Element Analysis (FEA) with 3-D 8-node linear stress/displacement elements. In this method the Fredholm integral is avoided and the force locations can be determined precisely without specific staining of the focal adhesions once the force field is obtained. The results have shown that our technique has force accuracy better than 0.06 nN and spatial resolution better than 5 microns with an objective lens of 10X. Accuracy and spatial resolution was easily improved to 0.03 nN and 3 microns by using a 63X water lenses. + Supported in part by the NSF-MRSEC program

3:15 PM Y5.5
A Continuum Treatment of Coupled Mass Transport and Mechanics in Growing Soft Biological Tissue.
Harish Narayanan[1], Krishna Garikipati[1], Ellen M. Arruda[1,2], Karl Grosh[1] and Sarah Calve[2]; [1]Mechanical Engineering, University of Michigan, Ann Arbor, Michigan; [2]Macromolecular Science and Engineering, University of Michigan, Ann Arbor, Michigan.

The growth of biological tissue depends upon the transport of molecules through the extra cellular matrix, and across cell membranes. The extra cellular fluid is the medium for transport through the matrix, while the molecules diffuse across cell walls, i.e. relative to the fluid. Transport in the tissue therefore has a multiscale aspect to it. Transport of the fluid relative to the matrix of the tissue has features in common with flow through porous media: it is driven by stress gradients in addition to concentration and chemical potential gradients. Therefore, the coupling of transport and mechanics plays a central role in the coarse scale process. In this talk we will present a treatment of this aspect of the problem in the context of continuum mixture theory. Thermodynamic consistency, the consequent restrictions on constitutive equations for transport and the relevant mechanical response of the tissue will be highlighted. The diffusion-reaction equations that govern the finer scale transport of molecules relative to the fluid will also be discussed. Several computational examples of a growing tissue will be presented to demonstrate the mathematical models. An engineered, *invitro*, tendon construct developed in our laboratory is the tissue of interest to us. The mathematical models will refer to this tissue and the computations will be in the same context.

3:30 PM Y5.6
Influence of Protein Structures on Mechanical Response.
Pijush Ghosh, Dinesh R. Katti and Kalpana S. Katti; Civil Engineering, North Dakota State University, Fargo, North Dakota.

Proteins are important for chemical and functional properties of biological materials. Proteins are also often suggested to play an important role in mechanical behavior of bio composites such as seashells and bones. The mechanical properties of a protein could be highly influenced by the structure of different domains constituting it. Thus structure plays a big role in the folding unfolding characteristics of protein and thus in its nature of resistance to external loads, which can potentially lead to toughness. Lustrin A, an important protein in nacre, the inner iridescent layer of seashells has abundance of β-sheets. The β-sheet of proteins when present close to each other in multiple numbers could take the shape of a planar β-sheath like structure or β-barrel to form a domain. In this work the mechanical response of β-planar sheaths and ?-barrels to external loads has been studied. The study is conducted on a spinach protein, Ferredoxin Reductase (1FNR). This protein has domains constituted of both β-planar sheaths and β-barrels. Loads of increasing magnitude are applied on the strands of these structures and the corresponding strains are measured Comparative studies of their stress-strain characteristics have been made to observe if the presence of any of these structures contributes to the enhanced mechanical response of nacre. These studies are conducted using steered molecular dynamics simulation. This paper deals with protein selection, simulation details, comparison of responses of β-planar sheaths and β-barrels, and presents possible deformation mechanisms when these protein domains are subjected to a wide range of mechanical forces.

3:45 PM Y5.7
Towards a Mechanical Model for Skin: Insights into Stratum Corneum Mechanical Properties from Atomistic and Coarse Grained Modelling of Lipid Organisation. Brendan O'Malley[1], David J. Moore[2], Massimo Noro[1], Jamshed Anwar[4], Becky Notman[4], Reinhold Dauskardt[3] and Eilidh Bedford[1]; [1]Unilever, Port Sunlight, United Kingdom; [2]Unilever, Edgewater, New Jersey; [3]Stanford University, Stanford, California; [4]Dept of Pharmacy, King's College, London, United Kingdom.

The outermost layer of skin, the stratum corneum (SC), provides the body with a physiologically essential barrier to unregulated water loss. Furthermore, the 15 to 20 micron thick SC, composed of heterogeneous lipid lamellae surrounding protein-rich corneocytes, is a complex composite structure that displays remarkable mechanical cohesion and integrity. To gain a detailed understanding of the contribution of SC lipids, cells, and their specific interactions to SC mechanical properties, requires building a complete mechanical model of the SC. In the current study we focus on modelling the hierarchical microstructure of the SC lipid phase, a matrix of ceramides, fatty acids and cholesterol, and relate this organisation to the mechanical properties of the SC. To investigate lipid packing, and its relation to

SC mechanical properties, we have employed a combination of atomistic molecular dynamics simulations and coarse-grained simulation methods. The latter method is parameterised using experimental data from FT-IR spectroscopy, X-ray scattering studies, and density profiles derived from the atomistic models. The atomistic models are used to probe the role of specific lipid species in maintaining the structural stability and cohesion of the SC extra-cellular matrix. Thus, for SC ceramides these models elucidate the strong hydrogen bonding networks that provide structural rigidity to the lipid matrix and mediate transformations between orthorhombic and hexagonal chain packing, as observed in both X-ray and FT-IR spectroscopy studies. To compliment the atomistic modelling, a coarse grained approach is used to investigate domain formation and lipid bilayer organisation, on length and time scales inaccessible with atomistic models. These coarse grained models display transitions between ordered hexagonal gel phases and disordered fluid phases, reproducing the experimentally observed ordering of the hydrophobic and hydrophilic regions. The above modelling approach is now being exploited to study altered SC mechanical properties, as induced by the presence of topically applied exogenous molecules (including water), and their relationship to changes in altered molecular organisation. In addition, the above models are being used to calculate the cohesive energy for lipid bilayer separation. This inter-lamellar cohesion is a critical component of desquamation process whereby controlled SC cohesive failure permits normal cell turnover. Future studies will continue to link mechanical models of the SC with mechanical experimental data from both in plane and out of plane measurements

4:00 PM Y5.8
Remodelling of Biological Tissue as a Process of Energy Minimization. Krishna Garikipati[1], Ellen M. Arruda[1,2], Harish Narayanan[1], Karl Grosh[1] and Sarah Calve[2]; [1]Mechanical Engineering, University of Michigan, Ann Arbor, Michigan; [2]Macromolecular Science and Engineering, University of Michigan, Ann Arbor, Michigan.

A developing tissue undergoes both growth and remodelling. We define growth as the addition or depletion of tissue mass. *Remodelling* is the evolution of the tissue's misrostructure at roughly constant mass. In this paper we will discuss a treatment of remodelling within the framework of continuum mechanics. For this purpose quantities that describe the microstructure are introduced. Among others these could include the orientation of collagen fibers in the matrix of tendons, variables that describe the network organization of collagen fibers, and the end-to-end length of protein molecules that can change their conformation. The Gibbs free energy of the tissue can be written as a functional whose arguments include the microstructural quantities and the deformation. The deformation is determined by the external loads and internal stresses and is governed by the usual equations of mechanics. Our hypothesis, drawing upon a fundamental thermodynamic notion, is that the microstructural state is determined by the tendency of the tissue to seek an equilibrium state, i.e. to minimize its Gibbs free energy. The idea that energy minimization drives the process of remodelling will be motivated by several examples from experimental biology. We will demonstrate a variational procedure by which the governing equations for microstructural remodelling can be obtained. These equations involve generalized thermodynamic driving forces and the Eshelby stress. Several analytic and numerical examples will be solved to demonstrate the evolution of tissue microstructure as governed by this process.

SESSION Y6: Poster Session
Tuesday Evening, November 30, 2004
8:00 PM
Exhibition Hall D (Hynes)

Y6.1
Molecular dynamics simulation of the effect of hydration on collagen stiffness. Uday Chippada and Dajun Zhang; Mechanical and Aerospace Engineering, Rutgers University, Piscataway, New Jersey.

The primary objective of the study is to analyze the effect of hydrogen bonds mediated by the structural water on the stiffness of collagen. A software called NAMD, coupled with the visualization program, VMD, is used for the simulations. It is a parallel molecular dynamics code designed for high-performance simulation of large bio-molecular systems. The Steered Molecular Dynamics (SMD) approach is used to study the mechanical properties of collagen-like peptides. The nodal data was obtained from the crystallographic results from the Protein Data Bank. Also nano-scale FEM was used, and it was found that structural water enhances the stability of triple helical peptides and hydrogen bonds stiffen the collagen-like peptides. SMD simulates the motion of atoms in a system of molecules over short intervals of time. The constant velocity pulling and the constant force pulling are considered. The change in the axial stiffness of collagen-like peptides in the presence or absence of water is calculated. The peptides are stretched to study the effect of hydrogen bonds. The variation of the stiffness with the change in amino acid sequence is calculated using NAMD. Segmental stiffness calculations are made, by stretching just the EKG segment and the POG segment of the triple helices. With ageing there is a gradual loss of water content in the bone, and by studying the effect of water mediated hydrogen bonds, diseases like Osteoporosis and Osteogenesis Imperfecta are better understood.

Y6.2
Mechanical Properties of Biomimetic Composites for Bone Tissue Engineering. Devendra Verma, Kalpana S. Katti and Bedabibhas Mohunty; Civil Engineering, North Dakota State University, Fargo, North Dakota.

A biomimetic process involving in-situ mineralization of hydroxyapatite (HAP) is used to design new composite biomaterials for bone tissue engineering. Surface and bulk properties of HAP composites have been studied for hydroxyapatite mineralized under two conditions, one in absence (ex-situ) of polyacrylic acid (PAAc) and other in presence (in-situ) of PAAc. XRD studies show existence of structural disorder in in-situ HAP. It has been observed that PAAc increases the rate of crystallization. FTIR studies indicate calcium deficiency in structure of both in-situ and ex-situ HAP. PAAc provides favorable sites for nucleation of HAP. During crystallization of HAP, PAAc dissociates to form carboxylate ion, which binds to HAP. Porous and solid composites of in-situ and ex-situ HAP with polycaprolactone (PCL) in 50:50 ratio have been made to evaluate their applicability as bone scaffold. Mechanical tests on solid samples suggest ex-situ HAP/PCL composites have higher elastic modulus (1.16 GPa) than in-situ HAP/PCL composites (0.82 GPa). However, in case of porous composites, in-situ HAP/PCL composites are found to have higher elastic modulus (29.5 MPa) than ex-situ HAP/PCL composites (10.4 MPa). Nanoindentation tests were also performed at different loads to evaluate extrinsic properties of both solid and porous composites. In-situ HAP using non-degradable polymers has thus shown to improve mechanical response in porous composites.

Y6.3
Influence of Mineral Content on Local Mechanical Properties of Cortical Bone. Laurent Henry[1], Alain Meunier[3], Marc Verdier[2] and Thierry Hoc[1]; [1]Ecole Centrale Paris, Chatenay Malabry, France; [2]LTPCM, Grenoble, France; [3]B2OA, Paris, France.

Several pathology produce abnormal microstructures and mineral contents involving very high fracture risks. For instance, in the case of the osteoporosis more one million of failure is recorded each year in Europe. If the decrease of the mineral density and the microstructural modifications associated with this pathology are the major reasons of the brittleness, the relations between these parameters are not yet completely understood. In particular, the clinical characterization is currently based on the only knowledge of the macroscopic mineral properties (dual-energy Xray absorption: DEXA, Ultrason in-vivo) which are not sufficient to predict the risk of fracture and require a better knowledge of bone tissues and their evolution. This study investigates the influence of mineral content on local strain. A compression sample of a bovine cortical bone exhibiting haversian microstructure was prepared. Compression test was performed with a specific micro-machine, the osteonal axis being orthogonal to the loading direction. Images have been taken with an optical microscope during mechanical test. In-plane strain field was computed using a micro-extensometry technique. An indicator of mineral content was obtained by SEM back-scattered electrons measurement. Linear regression was investigated between local strains and grey levels of SEM images. SEM grey levels were found to explain 45% of strain variation. Similar investigation performed at lower scale thanks to nanoindentation technique confirms our results with a correlation criterion close to 0.8 .

Y6.4
ZnO Doping in Calcium Phosphate Ceramics. Elizabeth Ann Withey[1,2] and Amit Bandyopadhyay[2]; [1]Materials Science and Engineering, Purdue University, Indianapolis, Indiana; [2]Materials Science and Engineering, Washington State University, Pullman, Washington.

Tricalcium phosphate (TCP) and hydroxyapatite (HAp) samples with varying concentrations of zinc oxide (ZnO) ranging from 0.5 wt.% to 3.5 wt.% were mixed and pressed using a uniaxial press. Green samples were sintered at 1250°C or 1300°C for 1 hr in a muffle furnace to understand the role of ZnO as dopants on densification and mechanical properties. Variation in the amount of ZnO present in TCP and HAp showed differences in the sintering behavior. At a sintering temperature of 1250°C both TCP and HAp experienced a continual increase in densification with increasing amounts of ZnO.

Doping of TCP with ZnO increased densification and microhardness over pure TCP. Samples sintered at 1300°C show lower densification and hardness than samples sintered at 1250°C. Analysis of microstructure using SEM revealed that grain size differed with amount of ZnO present in TCP and HAp. It was also found that ZnO was distributed evenly throughout the structures. Preliminary in vitro cell cultures were also done using OPC1 cells on ZnO doped substrates. It was noticed that substrates were non-toxic and cells grew uniformly over the substrates.

Y6.5
Substrate-Dependent Stiffness Gradients in M. Californianus Adhesive Plaques by Porosity Control. Scott Jewhurst[1] and J. Herbert Waite[2,1]; [1]Marine Science Institute, UC Santa Barbara, Santa Barbara, California; [2]Department of Molecular, Cell and Developmental Biology, University of California, Santa Barbara, California.

The marine mussel Mytilus californianus inhabits the nutrient-rich, but severely wave-swept intertidal zone, living as a sessile organism attached by an adhesive tether (byssus) to a substratum (rocks, pilings, other mussels, etc.). The byssus, consisting of an adhesive plaque, a thread, and the stem which links the byssus to the retractor muscles of the animal, is a sophisticated protein composite well designed for its task. Previous research has shown that the byssal thread is a functionally graded material, using tailored proteins to produce a gradient in the elastic modulus and yield behavior, of which one possible function is to mediate the modulus mismatch between the substratum (Ey 1 to 200 GPa) and the organism's retractor muscles (Ey = 0.2 MPa) to which the byssus is attached. Large, abrupt transistions in the elastic modulus would result in catastrophic stress concentrations when a load was placed on the thread, and may be mitigated by having a more gradual transistion in the elastic modulus. Recent research has discovered that the adhesive plaque, primarily consisting of a polymeric protein foam with seawater filled pores, is also a funtionally graded material which exhibits a porosity controlled stiffness (effective modulus) gradient between the substratum and the distal portion of the byssal thread. The porosity gradient of the plaque has also been determined to be tailored to the stiffness of the substratum, although the mechanisms by which the mussel regulates this process has yet to be elucidated. The plaque porosity is multifunctional, also serving as a hydration reservoir and may serve a shock-absorbing function by dissipating energy through capillary drag on the pore fluid during when a load is applied to the plaque.

Y6.6
Mechanical Response of Porous and Dense NiTi-TiC Composites. Douglas E. Burkes[1,2], Guglielmo Gottoli[1,2], John J. Moore[1,2] and Reed A. Ayers[2]; [1]Metallurgical and Materials Engineering, Colorado School of Mines, Golden, Colorado; [2]Center for Commercial Applications of Combustion in Space, Golden, Colorado.

The Center for Commercial Applications of Combustion in Space (CCACS) at the Colorado School of Mines is currently using combustion synthesis, or Self-propagating High-temperature Synthesis (SHS), to produce several advanced materials. These materials include ceramic, intermetallic, and metal-matrix composites in both porous and dense form. Currently, NiTi-TiC intermetallic ceramic composites are under investigation for use as a bone replacement material. The NiTi intermetallic has the potential to create a material that possesses both shape memory and superelastic properties while providing a surface that is capable of readily producing an oxide layer for corrosion resistance. The TiC ceramic has the potential to increase the hardness and wear resistance of the bulk material that can improve the performance lifetime of the implant. Processing parameters are critical to the production of the NiTi-TiC composite and will be discussed. These parameters can lead to the formation of substoichiometric TiC and nickel rich NiTi that changes the overall mechanical and material properties. In addition, the size of the TiC particles present within the bulk product varies with porosity. Both porous and dense samples have been mechanically analyzed employing nano- and micro-indentation techniques as well as compression tests in an attempt to characterize the mechanical response of these composites. The effects of the TiC particles and the formation of Ni3Ti intermetallic on the overall mechanical and material properties will be discussed.

Y6.7
The Chemical and Mechanical Properties of the Bio-halogenated Coating of the Nereis Jaws. Rashda Khan[1], Henrik Birkedal[1,4], Nelle Slack[3], Chris Broomell[2], Frank W. Zok[3], J. Herbert Waite[2] and Galen D. Stucky[1]; [1]Chemistry and Biochemistry, University of California, Santa Barbara, California; [2]Molecular, Cellular, Developmental Biology, University of California, Santa Barbara, Santa Barbara, California; [3]Materials Department, University of California, Santa Barbara, Santa Barbara, California; [4]Department of Chemistry, University of Aarhus, Aarhus, Denmark.

Jaws of a polychaete worm, Nereis (commonly known as a clamworm) are hard and abrasion resistant. Nereis hunts for prey in sand, when the prey is located the jaw-tipped proboscis (retractable muscle) is everted, thus allowing the victim to be firmly grasped. We have found that the jaw surface contains fluorine, chlorine, bromine and iodine as part of the inorganic components of this jaw. We have determined that acid hydrolysates of the whole jaw comprise of various post-translationally modified amino acids: dopa, halogenated histidine, tyrosine and cross-linked tyrosines. Several halogenated histidines and tyrosines have been characterized for the first time, including: dibromohistidine, bromoiodohistidine, bromoiodotyrosine, mono-chlorodityrosine, mono-chlorotrityrosine and dibromotrityrosine. Further, EDS has localized the halogens mainly to the outer coating of the jaw. Nanoindentation studies reveal that this outer coating of the jaw is distinctly harder than the core. The presence of fluorine has been confirmed in the jaw by XPS and 19F NMR studies. The halogen-rich surface displays unique mechanical properties and may serve as a protective coating. Halogens may enhance the resistance of proteinaceous material against decay by bacteria and fungi, given their role in other organisms. In this work the relationship of halogens to the chemical and mechanical properties of the Nereis jaws is described.

Y6.8
Byssal Thread: Inspired Biomaterial With Dopa and Metal Gradients. ChengJun Sun[1] and J. Herbert Waite[1,2]; [1]MCD Biology, UC Santa Barbara, Santa Barbara, California; [2]Marine Science, UC Santa Barbara, Santa Barbara, California.

Byssal threads are an important extraorganismic, extracellular connective tissue that enables robust substrate attachment for mussels in the intertidal zone. It is a longitudinally graded material in both mechanical properties and molecular composition. The fibrous core region of the thread is composed of two graded pre-collagens P and D (P dominates the proximal end and D dominates the distal end) and a non-graded NG. This core region is coated with a thin protective cuticle (thicker at the proximal end of thread) of which Mfp-1 (mussel foot protein-1) is a major structural component. Mfp-1 has 10-15 mole % Dopa (3,4-dihydroxyphenylanaline) that can participate directly in adhesion and cross-linking. Our data showed that Dopa concentration had a gradient distribution in Mfp-1 from different regions along the foot with the highest concentration from the Mfp-1 in the distal portion of the accessory gland. The distribution pattern of tyrosine had just the reverse trend. Meanwhile, the overall Dopa concentration in the thread decreased from the distal end to the proximal end of the thread. Since Dopa can auto-oxidize at neutral pH and tends to form iron catecholate complexes in the presence of FeIII, it is important to know about the iron distribution in the thread as well. Our EDS (Energy Dispersive X-Ray Spectroscopy) results showed that iron was mainly distributed in the cuticle region of the threads. Based on the calculation of volume fraction of the coating, Mfp-1 seems to be the major Dopa contributor in the thread and the Dopa distribution pattern seems to agree with the iron distribution. Since the distal portion of the thread is tougher, more exposed and subject to more abrasion than the proximal portion, our research suggests that Mfp-1 and its varying Dopa concentration could play an important role in enabling different parts of threads to exhibit specifically tailored mechanical properties.

Y6.9
A Novel Hydroxyapatite-based Scaffold with Optimized Mechanical Properties for Bone Repair. Yu Zhang[1], Hockin H. K. Xu[2], Shozo Takagi[2], Laurence Chow[2] and Brian R. Lawn[1]; [1]Materials Science and Engineering Lab, National Institute of Standards and Technology, Gaithersburg, Maryland; [2]Paffenbarger Research Center, American Dental Association Foundation, Gaithersburg, Maryland.

A major disadvantage of current orthopaedic implant materials, including sintered hydroxyapatite, is that they exist in a hardened form, requiring the surgeon to carve the graft to the desired shape. Calcium phosphate cement (CPC) powder, consisting of a mixture of fine particles of tetracalcium phosphate [TTCP: Ca4(PO4)2O] and dicalcium phosphate anhydrous [DCPA: CaHPO4], can be mixed with water to form a paste that can conform to osseous defects with complex shapes and set in vivo to form hydroxyapatite with excellent osteoconductivity. However, CPC has three major shortcomings: a relatively low strength; long setting time which may lead to washout of the CPC paste in vivo; and lack of macroporosity for bone ingrowth. In addition, the mechanical properties of scaffolds have become increasingly important in load-bearing applications, and the important microstructure-mechanical property relationships are not modeled for the macroporous scaffolds. Therefore, the present study aims to overcome the shortcomings of current CPC-based scaffolds, and to establish physical relationships between microstructure and mechanical properties. Chitosan (a biocompatible and biodegradable polymer) and mannitol (a water-soluble porogen) were incorporated into CPC: chitosan to render a stronger, fast-setting and anti-washout material; and mannitol to create macropores in CPC. After mannitol dissolution, CPC composites contained macropores of 50 to 200 mm in diameter and possessed mechanical properties matching those of cancellous bone. Resorbable Vicryl fibers of 300 micron in diameter and 8 mm in length were incorporated into the CPC composites to further boost the mechanical properties. The strengths of fiber-reinforced CPC composites approached those of cortical bone. This novel CPC-based graft system provides a model system to determine mechanical properties as a function of macropore volume fraction and fiber content, and hence to provide physically-based guidelines for design of superior scaffolds with engineered tissue responses.

Y6.10

A Redox-Active Matrix Protein From Mussel Byssal Threads. Jason Sagert and Herbert Waite; University of California, Santa Barbara, Santa Barbara, California.

Marine mussels make a proteinacous holdfast, known as the byssus, in order to attach themselves to substrates along rocky high-energy seashores. The threads or fibers comprising the byssus have a unique combination of mechanical properties that cannot be found in man made materials, including a self-healing ability following deformation, high toughness, a gradient in stiffness ranging from rubber at one end of each thread to nylon at the other. Recently, atomic force microscopy (AFM) has revealed new details about the organization of the preCOL, or Byssal Collagen proteins which are presumably the major tensile units in byssal threads. This data will be used to provide a context for the possible function of a novel protein that has been purified and partially characterized from the distal end of the thread. This protein is unique in that over 80% of the composition is represented by 3 amino acids: glycine, tyrosine (or Dopa), and asparagine, and no match can be found in the protein sequence database. A portion of the protein has been recombinantly expressed for antibody production and analysis of secondary structure. Although the function of the protein in the thread is not clear at present, experimental results obtained from the mechanical testing of wild threads and artificially oxidized threads are consistent with the protein possibly acting as a binding matrix that binds together the collagenous microfibrils in the thread.

Y6.11

Nanoscale Measurements of Water Loss During Desiccation of Biological Cell Suspensions. Surbhi Mittal and Ram Devireddy; Mechanical Engineering, Louisiana State University, Baton Rouge, Louisiana.

There is an urgent need to protect and conserve the endangered species of the world. Traditional programs of breeding and maintaining endangered species in captivity are not only very difficult but are also very expensive. Thus, limiting the genetic diversity of an endangered species. Desiccation, or the phenomenon of anhydrobiosis, offers the attractive possibility of storage at ambient temperature simplifying the logistics of storage and transportation thereby significantly reducing the cost. Cell stasis is achieved in nature by anhydrobiotic organisms through desiccation at ambient temperatures, and the pharmaceutical industry has made significant strides in storing proteinaceous drugs, membranes, and viral particles in dry state using various small sugar molecules as stabilizers. Although some success have been demonstrated in desiccation preservation of mammalian cells in the presence of sugars, the process has not been optimized due to a lack in understanding of the fundamental mechanism(s) by which sugars protect the cells. Current techniques of desiccation use a convective drying stage, an approach that has advantages both in terms of cost as well as ease of use operation. To dynamically quantify the rate of moisture loss during a prescribed desiccation protocol, we have modeled and characterized a novel micromembrane ultrasound (resonant) sensor. To model the sensor, we performed a static (stress) and dynamic (frequency change with change in imposed mass) analysis of the membrane. Rectangular membranes were selected for their structural/directional rigidity. Static analysis of the membrane was used to relate the stress induced in the membrane to the weight of the cell suspension. To prevent failure (rupture) of the membrane during the initial loading process, analytical and finite element techniques were utilized to determine the minimum dimensions of the membrane for a predetermined membrane material (silicon) and the loading weight (i.e. volume of the cell suspension). Dynamic analysis encompassed effects of the mechanical vibration i.e. the ultrasound vibrations, on the membrane with respect to time and change in loaded mass (i.e. loss of moisture content). Although the characterized device was found to have a sensitivity of 1 nanogram/millisecond, limitations in fabrication techniques and measurement/frequency analysis suggest that the fabricated device will only be able measure weigh loss in 10's of nanograms. We are currently fabricating the sensor using microfabrication techniques and in future, we expect to quantify the rate of water (moisture) loss during the drying protocol in the presence and absence of sugars. The results will be used to develop and perfect a computational model of water loss during drying of cells loaded with sugars. It is expected that these studies will form the basis for developing a desiccation protocol, for an easy and flexible solution for banking and storage of sperm cells from endangered species.

Y6.12

Electrophoresis on Flat Conducting Surfaces. Eli Mark Hoory, Jonathan Sokolov, Miriam Rafailovich and Vladimir Samuilov; Materials Science, SUNY @ Stony Brook, Stony Brook, New York.

Eli Hoory(SUNY Stony Brook), Jonathan Sokolov, Miriam Rafailovich, Vladimir Samuilov (SUNY Stony Brook) DNA electorphoresis on Conducting surfaces such as Aluminum, Nickel, and Indium Tin Oxide (ITO) has been studied. The objective was to minimize random charge biuld-ups that occurred on non-conducting surfaces in previous studies. Laser Scanning Confocal Microscopy was used to trace molecules of DNA labeled with a fluorescent dye, YOYO. We have found that mobility of DNA was approxiamately a factor of 3 times greater than that of oxide-coated silicon surfaces. We also observed single strands of DNA exiting droplets that were adsorbed to the ITO surfaces. The strands initially moved out radially from the drop and were then influenced toward the electric field. Support from NSF-MRSEC is gratefully acknowledged.

Y6.13

Measurements of Residual Stresses in Plasma-Sprayed Hydroxyapatite Coatings on Titanium Alloy. YungChin Yang, Physics, Academia Sinica, Taipei, Taiwan.

In an attempt to investigate the stress state and stress distribution in hydroxyapatite coatings (HAC), the residual stresses in thick HACs on titanium alloy were studied by the materials removal method, as a function of cooling media during spraying. In addition, and the x-ray diffraction sin2Ψ method was adopted as a comparison. The Young's moduli of hydroxyapatite coatings were measured on separated free coating by a three-point bending test. The results show that the measured Young's modulus of the HACs with an average of 22.8 GPa was found to be much lower than the theoretical value of bulk HA. During measurements by the materials removal method, on the three types of HACs using different cooling media, the interface between the HAC and Ti-substrate displays higher residual stress than the top surface of HAC. The residual stresses in all the HACs measured by both methods were in a compressive mode, and the residual stresses on the top surface obtained from the two methods are consistent. It was also found that the compressive residual stresses on the top surface of HAC and at the interface between the coating and the substrate both increased with increasing temperature of the HAC. Therefore, the coating temperature, and the effect of varying the cooling media during plasma spraying, had a significant effect on the residual stress states of the HACs.

Y6.14

Time-dependent Mechanical Behavior of Human Stratum Corneum. Kenneth S. Wu[1], Eilidh Bedford[2], David J. Moore[3] and Reinhold H. Dauskardt[4]; [1]Mechanical Engineering, Stanford University, Stanford, California; [2]Unilever Research and Development, Port Sunlight, United Kingdom; [3]Unilever Research and Development, Edgewater, New Jersey; [4]Materials Science and Engineering, Stanford University, Stanford, California.

The outermost layer of skin, or stratum corneum (SC), provides mechanical protection and a controlled permeable barrier to the external environment. The mechanical, fracture and debonding behavior of SC is crucial to its function and related to the underlying cellular and extracellular structure. Examination of the influences of temperature, hydration, topical applications and tissue treatments have received some attention, but investigations frequently ignore the underlying viscoelastic and molecular relaxation processes. These processes are systematically explored using dynamic and transient mechanical tests involving creep-recovery and stress-relaxation experiments to probe retardation and relaxation processes at short (high frequency) and long (low frequency) time scales. The influences of hydration, temperature, and chemical modification of the SC tissue were explored. Chemical treatment included delipidization and exposure to buffered pH solutions that have been shown to influence intercellular lipid properties. Time scales associated with SC viscoelasticity are reported and related to underlying molecular relaxation processes. Stretched exponential modeling of the behavior provides a measure of the distribution of relaxation time scales and their dependence on temperature, hydration, and other salient conditioning and loading parameters. Relaxation processes in the SC are shown to be dominated by long time scales with softening effects from increasing SC hydration significantly decreasing relaxation times. Implications for tissue treatments and emerging technologies that interface with skin are considered.

SESSION Y7: Mechanical Properties of Bio-Inspired and Biological Materials IV
Chairs: Kalpana Katti and Christopher Viney
Wednesday Morning, December 1, 2004
Room 205 (Hynes)

8:30 AM *Y7.1
Noninvasive Prediction of Fracture Risk due to Lytic Skeletal Defects. Brian Dale Snyder, [1]Orthopedic Surgery, Children's Hospital, Boston, Massachusetts; [2]Orthopedic Biomechanics Laboratory, Beth Israel Deaconess Medical Center, Boston, Massachusetts.

The skeleton is the third most common site of metastatic cancer and a third to half of all cancer cases metastasize to bone. While much has been learned about the mechanisms of metastatic spread of cancer to bone, little headway has been made in establishing reliable guidelines for estimating fracture risk associated with skeletal metastases. Our hypothesis is that a change in bone structural properties as a result of tumor-induced osteolysis determines the fracture risk in patients with skeletal metastases. Our goal was to develop an imaged based clinical tool to monitor the fracture risk associated with individual lesions in patients with skeletal metastases and to use this tool to optimize treatment and to monitor a patient's response to treatment. If bone is considered a rigid porous foam undergoing remodeling by osteoblasts and osteoclasts in response to local and/or systemic modulators of their activity, it follows that changes in bone material properties reflect the net effect of this remodeling activity. In a series of laboratory experiments we demonstrated that the reduction in the load carrying capacity of a bone with simulated skeletal defects could be predicted accurately and non-invasively using computed tomography. We also demonstrated that bone material properties from tissue excised from normal, osteoporotic and metastatic cancer bone specimens could be modeled analytically using a bivariate function of bone tissue density and bone volume fraction (Vvb). Since these bone specimens were inhomogeneous with respect to density distribution as is the case for pathologic bone in-situ, the sub-region with the minimum-Vvb accounted for more of the variability in the measured mechanical properties compared to the average Vvb for the entire specimen. Therefore the weakest subregion governed most of the mechanical behavior of the pathologic bone specimens. We applied our methods for predicting fracture risk to analyze bones from children with benign bone defects and showed that our relatively simple methods were much better at predicting fracture (100% sensitive, 94% specific) than current radiographic based guidelines (66% accurate). Using CT based data to calculate the load bearing capacity of vertebrae infiltrated with metastatic breast carcinoma, we also predicted with 100% sensitivity and 69% specificity the occurrence of a new vertebral fracture in women with metastatic breast cancer. These results are in contrast to the best available fracture risk criteria based on the size and location of the lesion on CT images of the spine, which were only 22% specific.Noninvasive image based method that measure both bone mineral density and whole bone geometry may also be used to monitor the response of skeletal metastases to anticancer treatment and to predict whether a specific lesion has weakened the bone.

9:00 AM Y7.2
Micro-Scale Physical and Chemical Heterogeneities in Biogenic Materials - Examples from Micro-Raman, Chemical Composition and Microhardness Indentation Measurements of Modern Brachiopod Shells. Erika Griesshaber[1], Reinhart Job[2] and Wolfgang W. Schmahl[1]; [1]Geology, Mineralogy and Geophysics, University of Bochum, Bochum, Germany; [2]Electrical Engineering and Information Technology, University of Hagen, Hagen, Germany.

Brachiopods are one of the most powerful tools for stable isotope paleotemperature analyses and the reconstruction of paleoenvironments. Their analytical popularity stems from the fact that they secrete low-magnesium-calcite shells, which are assumed to be precipitated in isotopic equilibrium with ambient sea water and are relatively stable in diagenetic environments. However, recent geochemical and isotope analyses reveal that even the secondary shell layer yields variable isotopic offsets from the expected equilibrium. We have investigated major and minor element concentration as well as microhardness variations of modern brachiopod shells with a spatial resolution between 40 to 80 microns. We can show that large chemical and hardness variations exsist within the shells. Inhomogeneity occurs not only between the primary and the secondary shell layer, but also within the secondary layer, and at distinct parts of the shell, such as the hinge, brachidium and foramen. Micro-Raman measurements were carried out on various positions of the primary and the secondary layer between the hinge and the tip of the shell. A reduction of the A1g Raman mode is observable towards the tip, changing from 1084 1/cm to 1083.5 1/cm. This most probably can be related to stress variations within the shells. The variation of the Raman shift is different on the upper and lower shell.

9:15 AM Y7.3
Lateral and Compressive Imaging of Cartilage Aggrecan via Atomic Force Microscopy as a Function of Ionic Strength. Lin Han[1], Delphine Dean[2], Alan J. Grodzinsky[3,4] and Christine Ortiz[1]; [1]Department of Materials Science and Engineering, Massachusetts Institute of Technology, Cambridge, Massachusetts; [2]Department of Electrical Engineering and Computer Science, Massachusetts Institute of Technology, Cambridge, Massachusetts; [3]Division of Biological Engineering, Massachusetts Institute of Technology, Cambridge, Massachusetts; [4]Department of Mechanical Engineering, Massachusetts Institute of Technology, Cambridge, Massachusetts.

Aggrecan macromolecules, the brush-like polyelectrolytes that make up the extracellular matrix of cartilage, have a unique macromolecular architecture composed of a dense array of highly negatively charged chondroitin sulfate glycosaminoglycan (CS-GAG) side chains attached to an extended core protein backbone. In this study, we have investigated the conformation and nanomechanical behavior of aggrecan using both lateral and compressive force measurements via atomic force microscopy (AFM). Bovine epiphyseal aggrecan (from Dr. Anna Plaas, USF, Tampa) was chemically end-grafted to micro-contact printed Au substrates with 15 μm hexagons; the region outside the hexagon had previously been functionalized with the self-assembling monolayer (SAM), 11-mecaptoundecanol, $HS(CH_2)_{11}OH$. The aggrecan surface density was measured to be 740$\pm$160 aggrecan molecules in 1μm$\times$1μm area by dimethylmethylene blue dye assay. Contact mode AFM images were taken across the aggrecan-grafted hexagons in NaCl aqueous solutions whose ionic strength ranged from 0.0001M-1M (pH=5.6) with a nanosized probe tip (30 nm in radius) that had been functionalized with the same OH-terminated SAM. With 2 nN of applied compressive force, a height of 281.1$\pm$14.1 nm at 0.0001M was observed to decrease nonlinearly with increasing applied compressive force down to 75.1$\pm$3.0 nm at 25 nN. Since the contour length, Lcontour, of a single aggrecan molecule is 400 nm, at 0.0001M the aggrecan molecules exist in a partially extended state ($0.7L_{contour}$) due to intra- and intermolecular electrostatic double layer repulsion between the CS-GAG side chains. As the ionic strength of the solution was increased to 1M, salt screening of the CS-GAG electrostatic forces caused the aggrecan layer height to nonlinearly decrease to 63.8$\pm$1.4 nm. Lateral force microscopy images showed that for a constant applied lateral displacement rate, the aggrecan layers exhibited a lower resulting shear force than the neighboring OH-terminated SAM under lower normal load (3 nN) and reversed behavior under higher normal load (20 nN) at 0.001M. The nonlinear dependence of aggrecan layer height and shear stress on normal load is different from that observed and predicted for linear polyelectrolyte brushes. Ongoing theoretical modeling of these data focus on simulating how the unique branched macromolecular architecture of aggrecan leads to novel electrostatic double layer repulsion profiles and conformational entropy changes depending on the solution conditions.

9:30 AM Y7.4
Nanoscale structural secrets and toughening mechanisms of natural seashell nanocomposites. Xiaodong Li[1], Patrick Nardi[1], Wei-Che Chang[1,2], Yuh J. Chao[1], Rizhi Wang[3] and Ming Chang[2]; [1]Department of Mechanical Engineering, University of South Carolina, Columbia, South Carolina; [2]Department of Mechanical Engineering, Chung Yuan Christian University, Chung-Li, Taiwan; [3]Department of Metals and Materials Engineering, University of British Columbia, Vancouver, British Columbia, Canada.

Nanoscale structure of the shells of Pectinidae and red abalone has been studied by SEM and AFM. Hardness and elastic modulus were measured by nanoindentation using a nanoindenter. Micro/nanoscale cracks were generated by microindentation using a microindenter. Nanoscale dynamic deformation behavior and fracture mechanics of these seashells were investigated using an in situ AFM tensile tester. Toughening mechanisms were discussed in conjunction of the architecture, hardness, elastic modulus, and energy-dissipation during cracking.

10:15 AM *Y7.5
Mechanical Properties of Nacre Constituents: An Inverse Method Approach. Francois Barthelat and Horacio D. Espinosa; Mechanical Engineering, Northwestern University, Evanston, Illinois.

Nacre, also known as mother-of-pearl, is the iridescent layer found inside some mollusk species such as oyster or abalone. It is made of relatively weak materials, but its hierarchical microstructure is so well optimized that its macroscopic mechanical properties are far superior

to those of its constituents. For this reason there is a great interest in nacre as a source of inspiration for novel designs of composites. Despite many years of research on nacre, an accurate characterization of its constituents is lacking. In this work nacre was tested as a layered composite material using low depth nanoindentation and uniaxial compression. The first test was modeled using finite element analysis and the second test was modeled as a Reuss composite in compression. A micromechanical model of the interface was also pursued to gain insight on the relevance of interface features such as tablet roughness and biopolymer hydrated response. The results of the two experiments were combined to solve an inverse problem that yielded the needed properties for both tablets and interfaces. These findings are expected to make possible computational models of nacre with a new degree of accuracy and therefore contribute to a better understanding of the mechanisms leading to its remarkable properties.

10:45 AM Y7.6
A Model of the Increased Elastic Compliance in Human Cancer Cells. Camilla Mohrdieck and Eduard Arzt; Max-Planck-Institut für Metallforschung, Stuttgart, Germany.

The internal structure and the mechanical behavior of cells can be changed substantially by biochemical reactions. In some human cancer cells they have been demonstrated to rearrange the internal cellular fiber network, called cytoskeleton, in such a way, that the initially isotropic fiber network forms dense ring-like structures around the nucleus whereas the peripheral regions of the cytoskeleton are depleted of fibers [1]. This change in the network topology is accompanied by an increase in the cellular elastic compliance by a factor of about 2. In this work we use an algebraic model to show that a topological change resulting in a decrease of the mean connectivity of the network leads to an increase in the number of unstable (i.e. soft) deformation modes making the fiber network more compliant. We support this explanation by simulating fiber networks with constant total fiber volume but different topologies ranging from isotropic structures to highly anisotropic ones with dense perinuclear rings. The simulations show that the elastic stiffness does indeed decrease as the number of perinuclear rings increases. This result indicates that cells make usage of dynamic changes in their cytoskeletons to actively control the number of unstable deformation modes and hence their overall stiffness. Further studies in this direction can therefore give more insight into the way cells self-assemble their internal fiber networks very fast and effectively. [1] M. Beil et al., Nature Cell Biology 5 (9) 2003

11:00 AM Y7.7
Characterization of DNA Flexibility using Quantitative Atomic Force Microscopy. Mark Edward Greene[1], Yael Katz[2], Jon B. Preall[2], Jon Widom[2,3] and Mark C. Hersam[1]; [1]Materials Science and Engineering, Northwestern University, Evanston, Illinois; [2]Biochemistry, Molecular Biology, and Cell Biology, Northwestern University, Evanston, Illinois; [3]Chemistry, Northwestern University, Evanston, Illinois.

The effect of base pair sequence on the bendedness and bendability of DNA was investigated using quantitative atomic force microscopy (AFM). Double stranded oligonucleotides containing multiples of sequences of six adenines (A-tracts) were used to create molecules with varying numbers of fixed bends. Single A-tract motifs have been shown to impart permanent bendedness to DNA molecules, and the sequence dependent mechanics may have a significant influence on nucleosome phasing and packing and gene regulation. Moreover, a relatively stiff polyelectrolyte such as DNA could be utilized in nonbiological contexts such as nanoscale systems requiring semiflexible tethers where the flexibility could be controlled by design by varying the base pair sequence. Inserts with zero, one, two, four, and six A-tracts were ligated into vector plasmid, then amplified using PCR resulting in five different molecules approximately 1000 base pair (bp) in length with the inserts flanked by 215 bp and 821 bp of plasmid DNA. The reverse primer was biotinylated at the end furthest from the insert to allow for the attachment of streptavidin functionalized gold nanoparticles. The DNA molecules were adsorbed onto freshly cleaved mica and imaged in air at 25°C using AFM operated in intermittent contact mode with silicon nitride cantilevers. A novel automated method of tracking contours from AFM images using a forward marching algorithm improves on manual point selection methods previously reported. Discrimination of the ends via direct visualization of the biotin as well as attachment of streptavidin functionalized gold nanoparticles was explored. The persistence length and moments of the end-to-end length and radius of gyration distributions were extracted from the contours and used to quantify the bendability and bendedness globally while curvature measurements were used to quantify the properties of the molecules locally. The data indicates a mean end-to-end length modulation of about 10 nm among the molecules, which is attributed to the presence of the varying number of A-tracts. The above quantitative methodology was also applied to DNA polymers with non-genomic repeats which demonstrate high binding affinity to histone octamer in the nucleosome. These large molecules are an order of magnitude longer than the A-tract molecules and provide an excellent point of comparison to examine the additional effect of excluded volume as well as polymer scaling. While this approach was applied to DNA, the methodology is general enough to characterize any polymer that can be imaged using scanning probe microscopy.

11:15 AM Y7.8
Mechanical Response of Malaria-Infected Human Red Blood Cells: Experiments. John P. Mills[1], Lan Qie[3], Ming Dao[1], Kevin S. W. Tan[4], Chwee-Teck Lim[3] and Subra Suresh[1,2]; [1]Dept of Materials Science & Engineering, MIT, Cambridge, Massachusetts; [2]Division of Biological Engineering & Affiliated Faculty of the Harvard-MIT Division of Health Sciences and Technology, MIT, Cambridge, Massachusetts; [3]Division of Bioengineering, National University of Singapore, Singapore, Singapore; [4]Department of Microbiology, National University of Singapore, Singapore, Singapore.

Malaria is one of the most widespread infectious diseases afflicting humans. Previous experiments involving either aspiration of infected cells into micropipette under suction pressure or deformation in laminar shear flow revealed that the malaria parasite Plasmodium falciparum could result in significant stiffening of infected red blood cells (RBCs). In this paper, we present optical tweezers studies of progressive changes to nonlinear mechanical response of infected RBCs at different developmental stages of the malaria parasite Plasmodium falciparum. From early ring stage to late trophozoite and schizont stages, up to an order of magnitude increase in shear modulus was found under controlled mechanical loading by combining experiments with three-dimensional computational simulations. These results, in conjunction with recent literature, suggest that stage-specific membrane proteins can significantly influence RBC deformability.

11:30 AM Y7.9
Microtubules Buckling and Bundling under Osmotic Stress: A Synchrotron X-ray Diffraction Study Probing Inter-Protofilament Bond Strength. Daniel J. Needleman[1], Miguel Ojeda-Lopez[1], Kai Ewert[1], Uri Raviv[1], Jayna Jones[1], Herbert Miller[2], Leslie Wilson[2] and Cyrus Safinya[2]; [1]Physics, materials, UCSB, Santa Barbara, California; [2]Molecular, Cellular, and Developmental Biology, UCSB, Santa Barbara, California.

Microtubules (MTs) are hollow cylindrical polymers composed of tubulin heterodimers that align end-to-end in the MT wall, forming linear protofilaments that interact laterally. MTs are crucial for a variety of cellular functions including cell division, cell structure, and intracellular motility. We introduce a probe of the strength of the inter-protofilament bonds within MTs and show that this technique gives insight into the mechanisms by which microtubule associated proteins (MAPs) and the cancer chemotherapeutic drug Taxol stabilize MTs. In addition, we present further measurements of the mechanical properties of MT walls, MT-MT interactions, and the entry of polymers into the microtubule lumen. These results are obtained from a synchrotron small angle x-ray diffraction (SAXRD) study of MTs under osmotic stress. Above a critical osmotic pressure, Pcr, we observe rectangular bundles of MTs whose cross-sections have buckled to a noncircular shape; further increases in pressure continue to distort MTs elastically. The Pcr 600 Pa, provides, for the first time, a measure of the strength of the lateral bond between protofilaments within a MT. The presence of neuronal MAPs greatly increases Pcr, while surprisingly, Taxol, which suppresses MT dynamics and inhibits MT depolymerization, does not affect the inter-protofilament bond strength. At higher osmotic pressures small stressing polymers may be forced into the MT lumen causing the MTs to revert to a circle cross-section and pack into hexagonal bundles. Within the hexagonal bundles, the spacing between MTs is controlled by the osmotic pressure, and this may be used to determine the interactions between MTs. This SAXRD-osmotic stress technique should find broad application for studying interactions between MTs and of MTs with MAPs and drugs.

SESSION Y8: Mechanical Properties of Bio-Inspired and Biological Materials V
Chairs: Kalpana Katti and Christopher Viney
Wednesday Afternoon, December 1, 2004
Room 205 (Hynes)

1:30 PM *Y8.1
Solving materials design problems in biology and technology - some case studies. Julian Vincent, Centre for Biomimetic and Natural Technologies, University of Bath, BATH, United Kingdom.

Biological materials are typically multifunctional, so it is not surprising that some functions should be intrinsically incompatible.

For instance many outer coverings are required to be both permeable and impermeable; examples are cell membranes, arthropod cuticle, plant roots, etc. In particular arthropod cuticle is called upon to provide a large number of functions, such as providing shape and structure, hinges, be a barrier, filter, etc. Some of these functions are intrinsically incompatible, although obviously since they coexist some form of compromise must have been evolved so that the cuticle can be multifunctional. Even so, these functions still represent basic conflicts in design, so it is possible that we can learn about the design process in materials from understanding the resolution of these conflicts, a method which has been pointed out several times, apparently first by Plato. More recently, Genrich Altshuller has used it in the development of one of the main tools in his system of inventive problem solving ("TRIZ" - Theoriya Resheniya Izobreatatelskikh Zadatch) which he and others in Russia developed as a design tool in engineering. The resolutions of the standardised conflicts which he recognised were derived from successful patents, and so represent a collection of engineering best practice. In comparing the resolutions provided from TRIZ with the resolutions to similar problems provided from nature, we are able to provide a measure of the similarity between technology and nature, and thus to test (a) whether the emerging study of biomimetics is likely to provide novel practical solutions to technical problems, and (b) how those solutions can be derived. Our studies show that the similarity between biological and technological solutions is of the order of 10%, and that biomimetics can therefore offer a truly novel approach.

2:00 PM Y8.2
Correlating Physical Properties of Staphylococcus Aureus with Antibiotic Resistance. Faith Marie Coldren[1], Nicole Levi[1], David L. Carroll[1], Richard Czerw[1], Jian Shen[2], Thomas Smith[2], Beth Smith[2] and Lawrence Webb[2]; [1]Center for Nanotechnology, Wake Forest University, Winston-Salem, North Carolina; [2]Department of Orthopaedic Surgery, Wake Forest University School of Medicine, Winston-Salem, North Carolina.

Staphylococcus aureus is implicated in 80% of human osteomyelitis and is also the primary cause of impetigo, endocarditis, and septic arthritis in humans. Dramatic increases in the percentage of clinically isolated S. aureus that are antibiotic resistant over the past decade indicate an alarming trend. S. aureus strains, with resistance to at least one antibiotic, have been emerging in a patient population with no associated risk factors for such infections. Treatment options for many antibiotic resistant S. aureus strains include the use of multiple antibiotics or, in the case of osteomyelitis, invasive surgery to physically remove the S. aureus. Alternative treatment options are likely to be necessary in the future. However, in order to create these options the physical structure of the bacterium needs to be correlated to antibiotic resistance. The topographical and structural components of S. aureus architecture of control strain NCTC 8325 and clinical isolates of S. aureus was investigated using atomic force microscopy in the force mapping mode and TEM. The whole cell elastic properties were determined using the Hertz model. Variations in topography and cell wall elastic modulus will be described for the control strain and clinical isolates and correlated with their minimum inhibitory concentration (MIC) to antibiotics methicillin and vancomycin. It is hoped that these correlations of physical properties of S. aureus with phenotypes can lead to non-antibiotic treatments and possible new diagnosis methods.

2:15 PM Y8.3
Analysis of the Facial Motion Using Digital Image Speckle Correlation. E. Guan[1], Sara Rafailovich-Sokolov[2], Isabelle Afriat[1], Miriam Rafailovich[1] and Richard Clark[3]; [1]Materials Science and Engineering, State University of New York, Stony Brook, Stony Brook, New York; [2]Stella K. Abraham High School, Hewlett, New York; [3]Biomedical Engineering, State University of New York, Stony Brook, Stony Brook, New York.

Usually based on holistic or structural matching methods, most facial recognition techniques utilize still images to characterize the features of the face. It is obvious that the shape, size, texture and relative locations of the facial features are extremely sensitive to the illumination, facial expression, point of view and especially modification of appearance by makeup, natural aging or surgery. This complicates the still image analysis and introduces uncertainty in identification. Video-based techniques with very low resolution have been developed to detect large facial motion, but mostly as an assistant to the feature extraction. Face of an individual is unique not only because of the appearance of the static features, but also the manner of the movement of these features. We suggest that it is possible to uniquely identify faces by analyzing the natural motion of facial features. In humans, facial muscles are directly connected to the skin. Therefore, detection of the motion of pores can in principal provide a projection of the motion of the underlying muscles. The measurement of motion is less prone to distortion by lighting conditions or obscured by facial makeup because the motion is determined by the facial musculature and skin elasticity. Digital Image Speckle Correlation (DISC) has long been used for the analysis of dynamic deformation on engineering materials. It can analyze two images taken before and after the subject is deformed and yields a displacement field of the subject surface by tracking of surface features such as the natural pattern produced by the texture of the skin pores. Results have shown that this non-contact, highly accurate, whole-field technique can measure facial deformation with very high spatial resolution from a large distance to the object. A total number of nine samples, among which two had disguise on, were tested in our experiment. Static facial recognition techniques failed attempting to identify the disguised ones. With the help of DISC technique, we have successfully recognized the samples in disguises by matching the smiling motion patterns. Our results have shown that the facial motion is intrinsic thus can be used as a signature for facial recognition. Although identical twins were born with identical facial muscles, they learn different way to use them in facial expressions during development. It is interesting to find that even though DISC method can pick up familial similarities in their movements, they produce distinctly different motion maps. Therefore, DISC can be a novel approach to distinguish twins. By examining the symmetry of the motion map, we also monitored the recovery procedure of a patient with mandibular fracture. Results indicate that potentially DISC can be a diagnostic tool for the facial muscle paralysis diseases such as Bell's palsy.

2:30 PM Y8.4
A Novel Dissimilar Material Joint Inspired from Tree Mechanics. Luoyu Roy Xu, Huacheng Kuai and Sreeparna Sengupta; Civil and Environmental Engineering, Vanderbilt University, Nashville, Tennessee.

Numerous studies have shown that failure often occurs at the interface between two dissimilar materials and improvement of interfacial properties can modify overall material behavior. Also, the interfacial strength based on current measurements is not an intrinsic material property because of the free-edge stress singularity. Therefore, we have attempted to develop a novel interface/joint design that will remove the stress singularity at bi-material corners. The proposed design, inspired by the shape and mechanics of trees, aims to produce valid interfacial strength data through an integrated theoretical, numerical and experimental investigation. Experimental results show that the tensile strength of the new joints increased by 50 % while the joint volume/area was reduced by at least 15 % compared to those of traditional butt joints. Results obtained from the finite element analysis indicates that for interfacial joint angles of 65 and 45 degrees, there is no stress singularity for most engineering materials. However, by varying the convex protruding length, the stress singularity seems to have been successfully removed and the interfacial normal stress is quite uniform in our new design. In-situ photoelasticity experiments also confirm these results. Thus, various combinations of interfacial joint angle and protruding length have a bearing on reduction of stress singularity at the interface. The proposed novel technique can be used in many engineering fields and is expected to have very broad impact. For example, 1. Composite repair to aging aluminum structures in aerospace engineering 2. Coating or painting of automobile structures, aircraft engine, ship structures 3. Teeth bonding and implant/bone joint in biomedical engineering 4. Using composite for civil structural rehabilitation 5. Ceramic/metal composite armor in defense engineering 6. Interfacial mechanical property characterization in material engineering 7. Thin film/MEMS design in mechanical engineering

2:45 PM Y8.5
Gecko Mechanics: Mimicking Biological Adhesion via Fibrillar Surfaces. Nicholas J. Glassmaker[1], Anand Jagota[1] and Chung-Yuen Hui[2]; [1]Lehigh University, Bethlehem, Pennsylvania; [2]Cornell University, Ithaca, New York.

Geckos and other lizards, as well as many species of insects, exploit arrays of tiny hair-like bristles to adhere to a variety of surfaces. In order to understand why such bristled fibrillar surfaces might offer advantages over corresponding flat ones, we examine the mechanics of fibrillar adhesion. We found that a single mechanical parameter controls the attachment strength of a fibril; this parameter depends on the surface materials and fibril diameter. Given a set of materials (e.g. gecko skin and tree leaf), one can obtain the maximum theoretical attachment strength only when the fibril diameter is very small. This is the case in nature, where it is observed gecko fibrils are typically 1 micrometer or less in diameter. Our theory is also supported well by quantitative experiments on a scale model synthetic system, where we observed increased work of fracture for fibrillar samples compared to flat ones. However, just making slender fibrils is not sufficient to produce a successful adhesive surface. Rather, several phenomena limit the fibrillar geometry: because of their small diameter, fibrils tend to adhere to each other and to buckle under compressive load. Both of these phenomena lead to poor contact behavior, and hence, we have derived mathematical conditions for avoiding them. These appear in the form of constraints on the fibril length, diameter, spacing, and material, and have been verified in experiments we performed on several synthetic fibrillar samples. Another effect that limits the effectiveness of an adhesive surface is roughness. While roughness often reduces the effective adhesion, some fibrillar surfaces are expected to be better suited to certain roughness profiles than corresponding flat surfaces. We have derived the average per fibril pull off force of a fibrillar array for a simple model of roughness that makes use of the Johnson Kendall Roberts (JKR) theory of adhesion. The results show that the pull off force depends on the standard deviation of asperity heights, fibril radius, and material properties (elastic modulus and surface interaction). In another more sophisticated model, we allow the fibril length (i.e. asperity height) and attachment strength to be statistically distributed. The results of this model show that the force to detach a fibrillar array is normally distributed, apart from a few exceptional situations. Closed form expressions are provided for the mean detachment force and variance, in terms of the fibril length and attachment strength distributions. We plan to perform experiments in the near future to assess the accuracy of each model.

3:30 PM Y8.6
Poro-Micromechanics of Bone: Impact Loading and Wave Propagation. Christian Hellmich[1] and Franz Ulm[2]; [1]Vienna University of Technology, Vienna, Austria; [2]Massachusetts Insitute of Technology, Cambridge, Massachusetts.

Once a continuum micromechanics model for the material under consideration has been developed and validated,poro-micromechanics allows for the quantification of poroelastic properties such as the Biot and Skempton coefficients. The tensor of Biot coefficients describesstress changes at the boundary of a material volume element in an isodeformation experiment, due to pressure increase in a fluid-saturated porous space within the material element. The tensor of Skempton coefficients describes the increase of pore pressure due to (homogeneous) stress applied at the boundary of a material volume element under undrained conditions, i.e. if no fluid mass can leave the pores. Both quantities are mandatory for understanding the mechanical behavior of fluid-saturated porous media, as e.g. osteoporotic bone. Employing a continuum micromechanics model for the transversely isotropic elasticity of cortical and trabecular bone, we determine the tensors of Biot and Skempton coefficients as functions of the volume fractions of mineral, collagen, and the micropore space (Haversian and Volkmann canals, and the inter-trabecular space). Increase of microporosity, as experienced in osteoporosis, as well as decrease of mineral content, as experienced in osteomalacia, lead to an increase of Biot and Skempton coefficients, i.e. to magnification of the mechanical role of the marrow filling the micropore space. For quantification of the marrow pressure rise upon downfall, undrained conditions are appropriate, as can be shown by model predictions of non-destructive impact experiments. Moreover, the aforementioned poroelastic properties enter the governing equations for wave propagation in anisotropic porous media. They allow for the prediction of undrained, fast and slow waves, as is verified by comparison of model results with experimental findings.

3:45 PM Y8.7
Finite Element Modeling of Bone Ultrastructure as a Two-phase Composite. Michelle L. Oyen and Ching-Chang Ko; University of Minnesota, Minneapolis, Minnesota.

Bone is a composite material with a mineral hydroxyapatite (HA) phase and an organic collagen-based phase. Each phase represents about half the material by volume. The precise arrangement of these components at the ultrastructural level is unclear but of great interest in understanding the mechanical functionality of bone. Nanoindentation tests show that the elastic modulus of bone is primarily distributed between 10 GPa and 30 GPa. In this study we examine different ultrastructural arrangements of collagen and apatite phases, to test different proposed models for bone composite ultrastructure within the same finite element modeling framework. Different configurations of the composite are considered, including (a) a compliant phase with stiff reinforcing particles, (b) a stiff phase with compliant reinforcing particles, and (c) an interpenetrating two-phase (co-continuous) composite. An elastic modulus of 100 GPa is used for the mineral phase and 100 MPa for the organic phase, with volume fraction of each phase fixed at 0.5. Stiff phase continuity (as the only continuous phase in 2D and 3D or as one of two continuous phases in 3D) gives rise to effective composite elastic modulus values of 25-30 GPa, similar to the experimental results. Isotropic models with compliant phase continuity only give rise to moduli around 300 MPa. Anisotropy was evaluated by calculating effective moduli in parallel and transverse directions relative to the primary axes of rectangular particles. High aspect ratio, stiff particles embedded in a compliant matrix do result in a substantially stiffened composite in the direction of the particles when compared to symmetric particles. However, this configuration results in a material with an effective elastic modulus of 2 GPa along the particle direction but a transverse modulus of only 250 MPa. Decreased interparticle spacing in the direction of loading was the mechanism for stiffening parallel to particle long axis, demonstrating an indirect effect of particle aspect ratio. Although many bone models have considered the mineral as a particle reinforcement phase, the current results suggest this arrangement would not give rise to a material with bone-like properties, particularly when transverse modulus is considered, regardless of the particle geometry. Some degree of continuity of the mineral phase is required for bone-like elastic modulus values and thus a partially to fully co-continuous ultrastructural arrangement of phases is supported. (Supported in part by NIH/NIDCR R21DE015410 and MDRCBB)

4:00 PM Y8.8
Characterisation of the Mechanical Behaviour of Trabecular Bone using Novel Techniques. Riaz Akhtar, Stuart Morse, Steve Eichhorn and Paul Mummery; School of Materials, University of Manchester, Manchester, United Kingdom.

The mechanical behaviour of macroscopic volumes of trabecular bone is a function of both the intrinsic properties of the bone and the 3-D architecture into which it is organised. The current study uses a combination of techniques (nanoindentation, tomography, and Raman spectroscopy) to provide both these components. The relative importance of each can then be explored by developing a reliable and realistic model of bone behaviour. Nanoindentation was used to probe the local mechanical behaviour of bovine and human trabecular bone under physiological conditions. Data were obtained from bone specimens from the hip of both species at 37C in simulated body fluid using a specially designed environmental cell. These data were used to form the constitutive relationships within a numerical, finite element model. The mesh for this model was formed directly from laboratory x-ray microtomography (XMT) images of trabecular bone. Laboratory XMT enables high spatial resolution (5 micron) non-destructive images of the internal architecture of the bone in 3-D to be obtained. Calibration of the x-ray attenuation for mineral content was performed by use of standards fabricated from differing hydroxyapatite contents. These standards were also used to calibrate the Raman spectroscopy system to enable the mineral content to be determined in bone specimens. Thus the mineral content of the bone could be included in the modelling. The architectures of the two bone types were characterised. The bovine bone had thicker trabeculae and a larger cell size than the human bone. In situ loading of the bone in compression whilst simultaneously imaging with tomography was performed. This enabled the deformation mechanisms in the bone to be studied. Typical stress/strain curves for open-cell materials were observed for both bone types. Initially, cell wall bending was observed. After additional strain, this mode changed to buckling with the onset of microcracking and permanent deformation. Finally, the cells were crushed. Differences between the bovine and human materials were noted. The bovine material had a higher yield strength and stiffness. This was due to the higher mineral content and trabeculae thickness. The increase in mineral content was determined by both tomography and Raman spectroscopy. Nanoindentation confirmed the higher intrinsic stiffness and strength of the bovine trabeculae. The use of these data in the finite element model enabled reliable predictions of the mechanical behaviour of the two bone types.

4:15 PM Y8.9
Normal Nanomechanical and Electrical Interaction Forces between Opposing Cartilage Aggrecan Macromolecules. Delphine Dean[1], Lin Han[2], Christine Ortiz[2] and Alan Grodzinsky[3,1,4]; [1]Electrical Engineering and Computer Science, Massachusetts Institute of Technology, Cambridge, Massachusetts; [2]Materials Science and Engineering, Massachusetts Institute of Technology, Cambridge, Massachusetts; [3]Biological Engineering Division, Massachusetts Institute of Technology, Cambridge, Massachusetts; [4]Mechanical Engineering, Massachusetts Institute of Technology, Cambridge, Massachusetts.

Aggrecan molecules from the extracellular matrix of cartilage are composed of 100 chondroitin sulfate glycosaminoglycan (CS-GAG) chains attached to a 300,000 kDa core protein in a bottle-brush-like structure. Electrostatic repulsion between the closely spaced (3-4 nm) negatively charged CS-GAG chains of densely packed aggrecan molecules within cartilage is a major determinant of the tissue's biomechanical properties, responsible for >50% of the compressive equilibrium modulus. In this study, the normal nanoscale interaction forces between opposing aggrecan macromolecules were measured as a function of separation distance using the technique of high resolution force spectroscopy (HRFS) in aqueous solutions of varied ionic strength (0.0001-1M NaCl). A dense, chemically end-grafted monolayer of bovine epiphyseal aggrecan (from Dr. Anna Plaas, USF, Tampa FL) was prepared on planar Au surfaces and Au-coated nanosized probe tips (end radius 50 nm) at the end of a soft cantilever force transducer. The success of the planar surface functionalization reaction was verified by advancing contact angle measurements (aggrecan=5±2°, Au=90±9°), dimethylmethylene blue dye assay (density = 740±160 aggrecan molecules per μm^2, molecular spacing = 37±4nm), and ellipsometry in ambient conditions (aggrecan height=7±1nm). The success of the probe tip functionalization was verified by the observation of consistent electrostatic double layer repulsive forces (via HRFS) when compressed against a neutral surface (i.e. Au functionalized with $HS(CH_2)_{11}OH$). On approach of the aggrecan-functionalized probe tip to an aggrecan-functionalized surface, large, long range electrostatic double layer repulsive forces were observed, beginning at tip-surface separation distances of 400 nm in 0.0001M NaCl. The magnitude of these forces was significantly larger and the range longer than that observed for either the aggrecan-functionalized probe tip or aggrecan-surface versus an opposing neutral surface, as well as for HRFS data between opposing chemically end-grafted CS-GAGs (molecular spacing 6 nm). The aggrecan vs. aggrecan force magnitude and range decreased as the NaCl concentration was raised from 0.0001M to 0.1M, but increased in both range and magnitude from 0.1 to 1M. These results reflect the unique branched macromolecular architecture of aggrecan, in which electrostatic interaction forces can modulate the conformation of both CS-GAGs, as well as the aggrecan core protein. Thus, changes in ionic strength may affect lateral as well as z-directed forces between and along the aggrecan brushes on the substrate and probe tip, all related to changes in constituent CS-GAG interactions and conformation.

4:30 PM Y8.10
Effect of Aging on the Toughness of Human Cortical Bone.
Ravi Kiran Nalla[1], Jamie J. Kruzic[1], John H. Kinney[2,3], Mehdi Balooch[3], Joel W. Ager[1], Michael C. Martin[1], Antoni P. Tomsia[1] and Robert O. Ritchie[1]; [1]Materials Sciences Division, Lawrence Berkeley National Laboratory, Berkeley, California; [2]Lawrence Livermore National Laboratory, Livermore, California; [3]University of California, San Francisco, California.

Age-related deterioration of both the fracture properties and the architecture of bone, coupled with increased life expectancy, are responsible for increasing incidence of bone fracture in the elderly. In order to facilitate the development of treatments which counter this increased fracture risk, a thorough understanding of how fracture properties degrade with age is required. The present study describes *exvivo* fracture experiments to quantitatively assess the effect of aging on the fracture toughness of human cortical bone in the longitudinal direction. Because cortical bone exhibits rising crack-growth resistance with crack extension, we depart from most previous studies by evaluating the toughness in terms of resistance-curve (R-curve) behavior, measured for bone taken from donors 34-99 years old. Using this approach, both the crack-initiation and crack-growth toughness are determined and are found to deteriorate with age; the initiation toughness decreases some 40% over six decades from 40 to 100 years, while the growth toughness is effectively eliminated over the same age range. Evidence from x-ray synchrotron tomography is provided to support the hypothesis that the reduction in crack-growth toughness is associated primarily with a degradation in the degree of extrinsic toughening, in particular involving crack bridging in the wake of the crack. Such observations are then correlated to changes at the ultrastructural level using Ultraviolet Raman Spectroscopy, Fourier Transform Infrared Spectromicroscopy and Atomic Force Microscope-based nanoidentation of individual collagen fibers. These results are important for an improved understanding of failure of cortical bone. This work was supported by the National Institutes of Health under Grant No. 5R01 DE015633.

SESSION Y9: Mechanical Properties of Bio-Inspired and Biological Materials VI
Chairs: Christian Hellmich and Franz Ulm
Thursday Morning, December 2, 2004
Room 205 (Hynes)

8:30 AM *Y9.1
Biomimetic Lessons: From Mother-of-Pearl to Mammalian Dental Tissues. Mehmet Sarikaya, Materials Science and Engineering, University of Washington, Seattle, Washington.

Organisms produce materials with physical properties that surpass those of analogous synthetic technological materials with similar phase compositions. Biological materials are highly organized from the molecular, to the nanometer, micrometer, and to the macro scale, often hierarchically providing an ordered continuity at all dimensional scales. Biological materials are simultaneously "smart," complex, self-healing, and multifunctional; they are fabricated in aqueous environments under mild conditions, using organic macromolecules that not only collect and transport the building blocks but also, consistently and uniformly, assemble them into ordered substrates and nuclei. Dynamics of these systems allows growth of new structures through molecular recognition and self-assembly, and also repair and replacement of old and damaged components. Biological materials are developed into intricate architectures in organisms from bacteria to the human body through eons of evolution. Rigorous correlation of structure-function of biological hard tissues at all dimensional scales is necessary for achieving robust structural design principles and for developing subsequent protocols for bionanofabrication of novel materials and systems based on biomimetic lessons. Using an array of structural characterization (from atomic force and electron microscopy to light optical microscopy) and mechanical testing tools (from nanoindentation to bulk bending), we examine three sets of hard tissues and draw biomimetic lessons: i. Mother-of-pearl of mollusks, with emphasis on nanomechanical properties of the hard and soft components (i.e., inorganic and proteinaceous layers) of the layered architecture; ii. Siliceous spicules of a deep-sea ocean sponge that have technological quality optical wave guide properties, and iii. Mechanical and structural coupling of mammalian dental tissues (dentin/enamel, and dentin/cementum). In all cases, the roles of both the soft and the hard components and their interface structures are examined for the fundamental understanding of these hybrid, complex, multifunctional composite systems.

9:00 AM Y9.2
Nanomechanical Mapping of Enamel Lesions.
Michelle Emma Dickinson and Adrian B. Mann; Ceramics and Materials Engineering, Rutgers The State University Of New Jersey, Piscataway, New Jersey.

Human dental enamel has a complex hierarchical structure consisting of nanoscale hydroxyapatite prisms arranged into prismatic clusters. The prismatic clusters are effectively long rods a few microns wide, but up to millimetres in length. The prisms and prismatic clusters are closely packed into an organic matrix to give the enamel's macroscale structure. In the oral cavity the exposed (occlusal) surface of the enamel is continually under fluctuating pH conditions due to dietary and bacterial changes. Under acidic conditions the enamel loses ions such as calcium and phosphate, which can be replenished by the buffering saliva once the pH increases. In localised areas the pH cycle maybe acidic for prolonged periods of time for instance due to the presence of acidogenic bacteria on the enamel's surface. This leads to the creation of a demineralised region called a carious lesion or white spot lesion because of it appears whiter than the surrounding enamel. Further exposure to low pH causes the structure of the lesion to degrade irreversibly and form a dental cavity or carie. Fortunately the formation of white spot lesions is reversible as ions diffuse in and out of the structure according to the local conditions. Re-mineralising treatments, such as the application of topical fluoride, can repair the demineralised structure and prevent a cavity forming. The mechanical properties of white spot lesions have been mapped using nanoindentation to measure elastic modulus (E) and hardness (H). These properties have been found to vary dramatically with depth below the occlusal surface. At the lesion's surface the E and H are relatively high at 102.9±18.5GPa and 5.06±1.12GPa respectively, however further into the lesion's interior these values can be as low as 1.38GPa and 0.02GPa, respectively, showing how the mechanical properties are severely reduced by the demineralisation process. The mechanical maps have been correlated with chemical composition maps obtained using x-ray microprobe and SEM. This shows how diffusion through the lesion is via structural 'channels' whose development appears to be closely linked to the longitudinal prismatic crystal structure of the hydroxyapatite. This understanding of a site specific diffusion route for demineralisation can lead to a more targeted approach for dental remineralisation treatments.

9:15 AM Y9.3
Microstructure of Brachiopod Shells - an Inorganic/Organic Fibre Composite Material with Nanocrystalline Protective Layer. Wolfgang W. Schmahl[1], Erika Griesshaber[1], Reinhart Job[2], Rolf Neuser[1] and Uwe Brand[3]; [1]Geology, Mineralogy and Geophysics, University of Bochum, Bochum, Germany; [2]Electrical Engineering and Information Technology, University of Hagen, Hagen, Germany; [3]Earth Sciences, Brock University, St. Cathrines, Ontario, Canada.

Brachiopods existed since the end of the proterozoic era and they are still extant today. They are one of the most intriguing phylae for evolutionary studies and their shells may serve as prototypes for the design of materials. We have investigated the microstructural (ultrastructural in biolological terminology) characteristics of the shell of the modern brachiopods Megerlia truncata and Terebratalia transversa by SEM, electron back scattering diffraction (EBSD), and microhardness indentation. The primary (outer) layer is a hard, nanocrystalline and dense Mg-calcite material. The inorganic component of the secondary (inner) layer consists of morphologically curved fibrous calcite single crystals. The fibres have spade-shaped cross-sections of 5 μm x 15 μm, and their length can exceed 100 microns. The fibres are stacked in parallel to form composite layers, and the direction of the fibre axis changes from layer to layer, frequently into perpendicular directions. The morphological fibre axis is perpendicular to the [001]-hex direction of the calcite structure, but arbitrary in the (001)-hex plane. Although the fibres have a curved outer shape, the crystallographic orientation is constant along the fibre. Locally, the crystallographic texture is a strong [001]-hex axial texture with no preferred orientation of the <100>-hex directions. The [001]-hex directions of the crystallites point perpendicular to the radius of curvature of the shell vault. Accordingly, the morphological fibre axis is parallel to the shell wall. The calcite fibres are coated with and separated by a thin protein layer which originates from the wall of the cell from which each fibre has grown. While the hardness of the nanocrystalline primary layer gives a mechanical protection against abrasives and attacking organisms, the fibre composite material of the secondary layer provides elasticity to the structure. The crystallographic texture optimises the material against cleavage-fracture of the calcite crystals.

9:30 AM Y9.4
Tribometrological Studies for Bioengineering. Norm Gitis, Center for Tribology, Inc., Campbell, California.

Bioengineered materials and coatings present a wide spectrum of durability challenges. Bones and muscles fail due to fatigue, wear and tear. Biological lubricants, including saliva, tears and synovial fluid, can dry up or deteriorate. Artificial hips, knees, elbows and fingers cannot yet fully mimic the functional and tribological performance of the biological joints. Artificial heart valves, blood pumps and kidneys require much testing and improvement. Ocular tribology deals with friction in contact lenses and eyelids, lubricated with tears and complicated by eye blinking. Durability of artificial teeth from porcelain, gold and acrylic has to be increased to the level of tooth enamel. Surgical needles and shaving blades have to maintain their sharpness so their cutting force stays low. Surgical sutures and cosmetic products should maintain low friction, balloons and stent grafts require good durability and flexibility. All these diverse tasks require much testing and understanding. The Bio-Mechanical Tester mod. UMT accommodates samples for a variety of biomedical applications, like testing bathroom tissues on skin, soap on skin, hydrogels, dental materials, surgical staples and sutures, medical needles, shaving blades, after-shave lotions, tooth pastes and tooth brushes, stent grafts and balloons, bio-fluids and bio-tissues. The UMT provides precision linear and rotational, including reciprocation, motions with programmable speeds and accelerations in the range from 0.1 micron/s to 10 m/s (8 orders of magnitude) and programmable positions (displacements) in the range from 0.5 micron to 150 mm (over 5 orders of magnitude). A load is controlled via a closed-loop servomechanism, and can be either constant or changing in the range from 10 micro-N to 1 kN (8 orders of magnitude). A number of parameters, including forces and displacements in all X, Y and Z directions, electrical contact or surface resistance, capacitance or impedance, deformation (elastic, plastic, creep) or wear depth, temperature, and contact acoustic emission can all be measured and recorded simultaneously. Also, built-in both optical and scanning force microscopy are available. The UMT has been utilized for both in-vitro testing on the artificial or cut-off skin and in-vivo testing on peoples arms, fingers and other body parts. Hip-simulating tests were performed on the UMT with in-situ monitoring tribological parameters of a hip joint. Both friction and acoustic emission have been confirmed sensitive to wear processes and can be used for in-situ wear monitoring during orthopedic life simulating tests. For testing medical needles and razor blades, the puncturing/cutting force into the skin and the depth of needle or razor penetration were measured. Plots of depth versus a number of punctures/cuts characterize how long needles or razors maintain their sharpness. Numerous tests showed effective evaluation of biomaterials for their tribological and mechanical properties, including abrasion and puncture resistance, elasticity, wear and friction, fatigue, hardness and scratch resistance, all with the single multi-sensor instrument.

10:15 AM Y9.5
Independent Control of Mechanical Rigidity and Toughness of Hydrogels. David J. Mooney[1,2,3] and Hyun Joon Kong[1]; [1]Department of Biological and Materials Science, University of Michigan, Ann Arbor, Michigan; [2]Department of Chemical Engineering, University of Michigan, Ann Arbor, Michigan; [3]Department of Biomedical Engineering, University of Michigan, Ann Arbor, Michigan.

Refined control over the mechanical properties of hydrogel-based materials formed from cross-linking between polymers has been increasingly regarded to be critical for their application. In general, increasing the cross-linking density (ρ) of polymer gels raises the mechanical rigidity, but makes the gels more brittle. We proposed that stepwise energy dissipation in hydrogels formed from natural macromolecules could provide a mechanism to decouple the dependency of the mechanical stiffness and toughness from ρ of the gel. Alginate hydrogels were chosen as a model system, because alginate can be gelled via ionic or covalent cross-linking, and its block structure dictates the structure of ionic cross-links. Increasing ρ of the gels formed using covalent cross-linking raised the elastic modulus (E), but led to a reduction in the fracture energy (W) of the gels. In contrast, increasing the number of ionic cross-links and length of blocks responsible for the cross-linking raised both E and W. Oscillatory shear measurements revealed that ionically cross-linked blocks are capable of dissipating the deformation energy, leading to their partial and stepwise dissociation with the increase in extension. In contrast, covalently cross-linked points accumulate the energy, leading to the catastrophic breakage at small extension. From the results of this study, we could demonstrate a novel approach to regulate different mechanical properties of gels in an independent manner. This study provides valuable guideline to the design of a broad array of polymer hydrogels.

10:30 AM Y9.6
Wear Mechanisms of Untreated and Gamma Irradiated UHMWPE used in Joint Replacements. Jing Zhou and Kyriakos Komvopoulos; Mechanical Engineering, University of California, Berkeley, Berkeley, California.

Wear of ultra-high molecular weight polyethylene (UHMWPE) presents a serious clinical obstacle limiting the longevity of the joint implants. In particular, the generation of fine wear debris leads ultimately to osteolysis and eventual implant loosening, thereby necessitating revision surgery. Recent investigations have indicated that structural modification of the UHMWPE component is imperative to the increase of the wear resistance of orthopaedic implants. The identification of the initial wear mechanisms of untreated and gamma irradiated UHMWPE sliding against CoCr alloy in bovine serum was the objective of this study. The strong correlation between wear resistance and gamma irradiation dose indicated a strong effect of microstructure changes due to gamma irradiation on the wear behavior of UHMWPE. Fibril formation, delamination, micropitting, and regularly spaced folds (with average spacing controlled by the irradiation dose) were found on the wear tracks. Surface folding is attributed to surface plastic flow and the degree of mobility of the crystalline lamellae. Irradiation-induced crosslinking prevents chain alignment parallel to the surface during sliding and surface folding increases the resistance against surface plastic shear. These two synergistic effects are responsible for the increased wear resistance of gamma irradiated UHMWPE. A deformation model, derived based on the experimental evidence of the surface and subsurface morphology and texture evolution, is used to interpret the effects of crosslinking and lamellae rearrangement on surface folding.

10:45 AM Y9.7
Design of High Strength Degradable Polyphosphazenes: Modulation of Mechanical Properties via Side Chain Chemistry. Sethuraman Swaminathan[4,1,7], M. Nguyen[3], Lakshmi S. Nair[4], A. Singh[5], H. R. Allcock[5], Y. Greish[6], P. W. Brown[6] and Cato T. Laurencin[1,2]; [1]Dept of Chemical Engineering, University of Virginia, Charlottesville, Virginia; [2]Dept of Chemical Engineering, Drexel University, Philadelphia, Pennsylvania; [3]Department of Biology, University of Virginia, Charlottesville, Virginia; [4]Dept of Orthopaedic Surgery, University of Virginia, Charlottesville, Virginia; [5]Dept of Chemistry, Pennsylvania State University, University Park, Pennsylvania; [6]Intercollege Materials Research Laboratory, Pennsylvania State University, University Park, Pennsylvania; [7]Dept of Biomedical Engineering, University of Virginia, Charlottesville, Virginia.

Polyphosphazenes are linear, high molecular weight, inorganic-organic polymers, with a backbone consisting of alternate phosphorous and nitrogen atoms with each phosphorous atom linked to two organic side groups[1].Polyphosphazenes having amino acid ester side groups are hydrolytically unstable forming non-toxic and neutral degradation products and therefore form potential candidates for various biomedical applications[2].It has been found that these side groups play a crucial role in determining the physical, chemical, degradation and thermal properties of the corresponding polyphosphazenes.The objective of the present study was to evaluate the effect of the structure and chemistry of various side groups on the mechanical properties of corresponding amino acid ester polyphosphazenes. Amino acid ester single substituent polymers such as of poly[bis(ethyl glycinato) phosphazene](PNEG) and poly[bis(ethyl alanato) phosphazene](PNEA) and mixed substituent polyphosphazenes having different ratios of alanato side groups along with other aromatic side groups such as poly[(ethyl alanato)(p-methyl phenoxy)phosphazene](PNEA/mPh), poly[(ethyl alanato)(phenyl phenoxy)phosphazene](PNEA/PhPh) and poly[(ethyl alanato)(ethyl tyrosinato) phosphazene](PNEA/ET) were used in the present study. All the polymers were synthesized and characterized according to reported procedures[1].Cylindrical matrices of these polymers (diameter 5mm and height 10mm) with n=6 were fabricated and mechanical properties were measured using Instron (Model 5544, Instron Inc., MA). The *endash*—P=N− backbone of polyphosphazene is highly flexible and hence the structure and compactness of side groups can have significant effect on the physical and mechanical properties of the polymer.Among the polymers studied, PNEG has the poorest compressive properties with a compressive modulus of 15.8±7.34 MPa.The use of alanato side groups on the other hand was found to significantly enhance the thermal as well as the mechanical properties of PNEA (185.7±77.1 MPa).This can be attributed to the bulkier ethyl alanato groups in PNEA that restrict backbone motion compared to glycinato groups and results in a more rigid polymer.Similarly, it has been found that the incorporation of aromatic side groups could significantly affect the mechanical properties of the polymers depending on the nature and ratio of the side groups present.This has been systematically correlated to various factors that affect polymer backbone flexibility in these polymers. The present study is the first of its kind to systematically investigate the effect of side group chemistry on the mechanical properties of biodegradable polyphosphazenes.These studies will enable the design and synthesis of novel polymers with well-controlled mechanical properties for specific application. NIH Grant# 46560 1. Allcock. Chemistry & Applications of Polyphosphazene, Wiley Interscience, 2003. 2. Lakshmi S, et al. Adv Drug Delivery Rev 2003;55:467-82.

11:00 AM Y9.8
Structure, Rheology, and Release Characteristics of Poly(lactide)-poly(ethylene glycol)-poly(lactide) Hydrogels.
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Biodegradable and biocompatible polymers made from poly(lactide) have attracted attention recently because of their ability to form hydrogels, which has potential applications in drug delivery and tissue engineering applications. We have investigated the microstructure and rheology of aqueous solutions and gels comprised of poly(lactide)-poly(ethylene oxide)-poly(lactide) triblocks. Through mechanical rheology we have shown that these gels have elastic moduli greater than 10,000 Pa. This value of elastic modulus is in the same range as several soft tissues, making these materials excellent candidates for a variety of tissue engineering applications. Moreover, the value of the elastic modulus strongly depends on PLLA block length, offering a mechanism to control the mechanical properties as desired for particular applications. We have also performed comparative study of PLA-PEO-PLA copolymers where the PLA block has been made from crystalline L-lactic acid (LLA) versus those made from a mixture of D and L lactic acid (DLLA), which is amorphous. The gels made from DLLA blocks have elastic moduli almost an order of magnitude less than those made from LLA blocks, again offering a molecular handle to tune the rheology for specific applications. Dynamic light scattering shows that the triblocks form aggregates in dilute solutions with hydrodynamic diameters in the range of 50-130 nm. The aggregate size increases as the size of the PLA block increases, and also is larger for the PLLA triblocks as compared to the PDLLA systems. SANS spectra on the gels, however, shows no evidence of micelles. The data obtained is consistent with formation of large-scale aggregates that are polydisperse and ill-defined. Finally, drugs with varying hydrophobicity were dissolved along with these polymers in water to physically entrap it in the gels and polymer solutions. The drug release profile obtained for the more hydrophilic drugs (e.g methyl paraben), shows an almost zero order release behavior that continues slowly and steadily over the entire period of release. However for the more hydrophobic drugs (e.g. indomethacin), a reservoir-like release was seen, which continued over a period of several hours. The rate of release was also found to strongly dependent on the chemistry of the PLA block and the hydrophobicity of the drugs.

11:15 AM Y9.9
Mechanical Behavior of Ceramic / SAM Bilayer Coatings.
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Ceramic/self-assembled monolayer (SAM) bilayer coatings can provide adequate protection and/or act as a multipurpose coating for microelectronics and MEMS applications, due to synergistic effects by forming the hybrid coating structure. The organic SAM layer acts as a 'template' for the growth of the ceramic layer (biomimetic process) while the hard ceramic layer can provide protection from environmental and mechanical impact. To process the bilayer coatings, a low-temperature solution deposition technique is employed using phosphonate-based SAMs and zirconia precursors. A particulate ceramic film is formed by an enhanced hydrolysis of zirconium sulfate ($Zr(SO_4)_2{\cdot}4H_2O$) solutions in the presence of HCl at about 80°C, and its particle size and thickness effects will be discussed. In addition, microstructure and micromechanics involved in the synthesis and processing of both ceramic and SAM coatings are systematically assessed in an attempt to establish the structure-property relations of the bilayer coatings. Especially, mechanical properties of the coatings such as elastic modulus and hardness are analyzed at nano- and microscales using a combined nanoindenter/AFM system as well as with the aid of theoretical models. Further, the substrate effects resulting from a large indentation depth relative to the film thickness will be isolated to obtain the 'film-only' properties. This study will highlight the role of a compliant SAM layer to form a strain-tolerant bilayer coating that is a prerequisite for the aforementioned applications.