

# Modeling and simulation of the mechanical behavior of hierarchical bovine enamel

Swantje Bargmann<sup>1,2</sup>, Ingo Scheider<sup>1</sup>, Tao Xiao<sup>1</sup>, Ezgi Yilmaz<sup>3</sup>, Gerold Schneider<sup>3</sup>, Norbert Huber<sup>1</sup>

<sup>1</sup> Institute of Materials Research, Materials Mechanics / ACE-Centre, Helmholtz-Zentrum Geesthacht, Germany

<sup>2</sup>Institute of Continuum Mechanics and Materials Mechanics, Hamburg University of Technology, Germany

<sup>3</sup>Institute of Advanced Ceramics, Hamburg University of Technology, Germany

Dental enamel is the outermost layer of a tooth crown consisting of a hierarchical and graded structure. Approx. 85 vol. % of enamel consists of the mineral hydroxyapatite mineral, the rest being protein and water. The hierarchical organization of bovine enamel can be characterized in 3 different levels. Mechanical properties such as stress-strain behavior or the elastic modulus differ greatly on different hierarchical levels. This contribution is concerned with the modeling and computation of the mechanical behavior, in particular with the failure, of the enamel of a bovine tooth. The model [1] accounts for non-linear, large-deformation kinematics, linear viscosity and softening at each level, i.e. at each scale. The numerical implementation is carried out with the help of the finite element method. A complex microstructure representing bovine enamel is studied in the multiscale numerical examples. The results capture major features of the physical experiments, such as nonlinear stress-strain behavior, stiffness and failure strength.

[1] S. Bargmann, I. Scheider, T. Xiao, E. Yilmaz, G. Schneider, N. Huber, *Comput. Mater. Sci.*, **79**, 390, (2013)

[2] H. Yao, H. Gao, *Int. J. Solids Struct.* 44 (25–26) (2007) 8177–8193

[3] H. Gao, *Int. J. Fract.* 138 (2006) 101–137

## **Correlating the Free-Volume Evolution to Plastic Deformation of Highly Cross-Linked Polymers from Large Scale Coarse-Grained MD Simulations**

Amin Aramoon<sup>1</sup>, Stephen A. Barr<sup>2</sup>, Timothy D. Brietzman<sup>2</sup>, Jaafar A. El-Awady<sup>1</sup>

<sup>1</sup> Department of Mechanical Engineering, Johns Hopkins University, Baltimore, MD  
<sup>2</sup> Air Force Research Laboratory, Wright-Patterson AFB, OH

Highly cross-linked polymer networks (e.g. epoxies) are widely used in many automotive, marine, and aerospace applications. Predicting the damage and failure of such systems is of crucial interest for the reliable performance of these class of materials. The evolving free volume (voids) in these networks under loading plays a critical role in both their elastic and plastic response. Macroscopic properties such as elasticity, glass transition temperature, and failure can be experimentally determined. In addition, the distribution and size of free volumes can be measured using positron annihilation techniques. However, in such studies it is not always easy to identify the micro-structural features controlling plasticity and failure. On the other hand, numerical methods such as quantum mechanics (QM) and molecular dynamics (MD) simulations can shed light on the atomic processes involved, but are computationally expensive and limited to modelling extremely small volumes, and further linking the outcome of these methods with continuum models still requires further developments.

In this work, a MD coarse-grain model has been developed to study the plastic behavior of epoxy materials. The polymerization of a highly cross linked polymer network in different curing conditions such as temperature, cross-linker functionalities and degree of cross linking are studied using a dynamic cross-linking algorithm. The effect of chain size, length of monomers, and degree of cross-linking on the evolution of the free volume density and subsequently plastic deformation (e.g. hardening and failure). Free volumes are measured by fitting unit volume cells in the network. From these simulations we also develop a direct correlation between the evolution of plastic deformation and the free volume density of the epoxy.

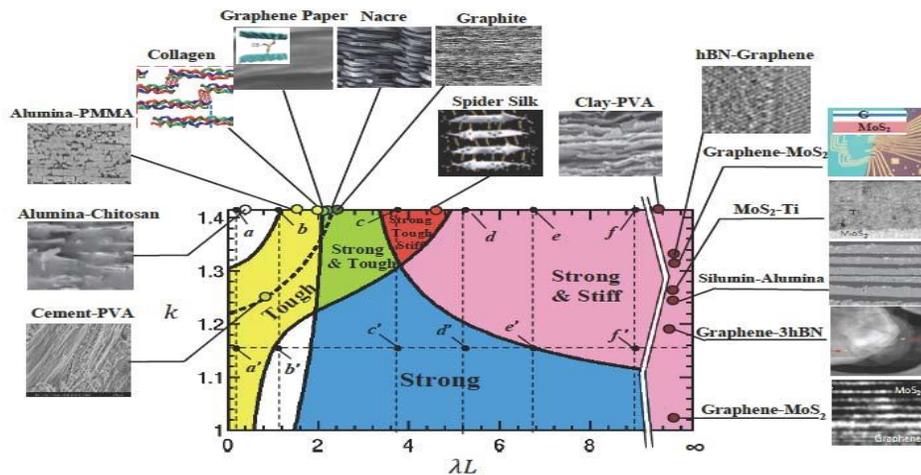
# Universal Structure-Material-Property Map for Natural and Biomimetic Platelet-Matrix Composites and Stacked Heterostructures

Navid Sakhavand<sup>1</sup> and Rouzbeh Shahsavari<sup>1,2</sup>

<sup>1</sup> Department of Civil and Environmental Engineering, Rice University, Houston, TX 77005

<sup>2</sup> Department of Material Science and NanoEngineering, Rice University, Houston, TX 77005

Many natural and biomimetic platelet-matrix composites -such as nacre, silk and clay-polymer -exhibit a remarkable balance of strength, toughness, and/or stiffness, which call for a universal measure to quantify this outstanding feature given the structure and material characteristics of the constituents. Analogously, there is an urgent need to quantify the mechanics of emerging electronic and photonic systems such as stacked heterostructures, which are composed of strong in-plane bonding networks but weak interplanar bonding matrices. Herein, we present the development of a unified framework to construct a universal structure-material-property diagram that decodes the interplay between various geometries and inherent material features in both platelet-matrix composites and stacked heterostructures in the shear mode. Validated by several 3D-printed specimens and a wide range of natural and synthetic materials across scales, this universally valid diagram (Figure 1) has important implications for science-based engineering of numerous platelet-matrix microstructures and stacked heterostructures while significantly broadening the spectrum of strategies for fabricating new composites through incorporating contrasting platelets. Given the conference theme of “Microstructural Frontiers”, this work opens up several new opportunities to further extend the proposed diagram to include inelasticity, locking mechanisms, stacked multiheterostructures, extrinsic hierarchical toughening processes, etc. to identify and delineate new boundaries and overlaps in mechanistic processes of platelet-matrix microstructures with the goal of unveiling other mysteries in multi-phase multi-functional materials.



**Figure 1.** Universal Structure-Material-Property Map for Platelet-Matrix Composites and Stacked Heterostructures

Figure 1. Universal Structure-Material-Property Map for Platelet-Matrix Composites and Stacked Heterostructures

[1]. N. Sakhavand, R. Shahsavari, Langmuir, 29, 8154 (2013)

[2]. N. Sakhavand, R. Shahsavari, Nature Materials, In review (2014).

## Scaled dynamics of nanoparticles in semi-dilute polymer solution

Sudipta Gupta<sup>1</sup>, Michael Ohl<sup>1</sup>, Ralf Biehl<sup>2</sup>, Margarita Krutyeva<sup>2</sup>, Dieter Richter<sup>2</sup>

<sup>1</sup>JCNS-SNS-Oak Ridge National Laboratory, Oak Ridge, TN 37831, USA <sup>2</sup>JCNS-1 and ICS-1, Forschungszentrum Jülich, 52425 Jülich, Germany

In recent times the diffusion of nanoparticle in complex polymeric fluids has proven to be of considerable importance in understanding the underlying dynamics of the solvent itself [1] and is of immense technological interests, like chromatography, electrophoresis, and drug delivery. In this regard, one can understand biological phenomena involving transport of proteins through a media consisting of concentrated biopolymer like DNA or through polysaccharide solutions. The novelty of such process also lies in detail understanding of colloidal diffusion [2] and sedimentation through a solution of non-adsorbing polymer chains, such as polymer solutions [3], melts [4], bio-macromolecular solutions [5], cells and colloid suspensions [6]. In these connection passive microrheological measurements [7] provides important information about the local/internal viscoelastic properties.

We used two independent systems consisting of human globular protein in an aqueous solution of Poly(ethyleneoxide)(PEO) and POSS hybrid plastic nanoparticles in a Polyethylene (PE) Xylene solution implementing state of the art neutron spin echo (NSE) and pulsed field gradient-NMR (PFG-NMR) technique to study the dynamics of the nanoparticles in semi-dilute polymer solution. Following the recent scaling predictions by Cai et al. [1] We found power law dependency of the normalized terminal diffusion coefficient ( $\bar{D}_t/D_s$ ) to the polymer volume fraction ( $\phi$ ) where  $D_s$  is the particle diffusion coefficient in pure solvent. Using both PFG-NMR and NSE we found  $\bar{D}_t/D_s \sim \phi^{-1.52}$  dependency in the intermediate scaling regime  $\xi(\phi) \leq d \leq a(\phi)$  and  $\phi_d^\xi \leq \phi \leq \phi_d^a$ , where  $\xi$  is the correlation length or the polymeric mesh size,  $d$  diameter of the probed nanoparticle and  $a(\phi)$  is the concentration dependent tube diameter of the corresponding polymer solution (Fig. 1),  $\phi_d^\xi$  and  $\phi_d^a$  are the crossover concentrations at which the concentration dependent correlation length  $\xi(\phi)$  and tube diameter  $a(\phi)$  becomes equal to the particle size ( $d$ ). Both NSE and PFG-NMR reveals the presence of a fast and slow diffusion mode, which has been identified as diffusion inside and outside of the mesh.

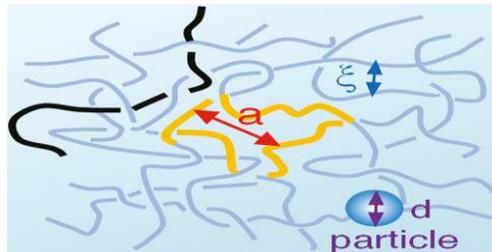


Fig. 1: From reference [1]. Schematic representation of a particle of size “d” in polymer solution.

- [1] L. H. Cai et al., *Macromolecules*, **44**, 7853 (2011).
- [2] D. Gold et al., *Macromolecules*, **29**, 5700 (1996).
- [3] R. A. Omari et al., *Phys. Chem. B.*, **113**, 8449 (2009).
- [4] H. Y. Guo et al., *PRL*, **102**, 075702, (2009).
- [5] J. Liu et al., *PRL*, **96**, 118104, (2006).
- [6] T. G. Mason et al., *Mol. Struct.*, **383**, 8190. (1996).
- [7] T. G. Mason et al., *PRL*, **74**, 1250, (1995).

## **Welding and healing of polymer interfaces: Connecting structure, dynamics and strength**

Mark Robbins<sup>1</sup>, Ting Ge<sup>2</sup>, Gary Grest<sup>3</sup>

<sup>1</sup>Johns Hopkins University, USA

<sup>2</sup>University of North Carolina, USA

<sup>3</sup>Sandia National Laboratory, USA

Applying heat to polymer interfaces is a common means of welding polymer components or healing cracks in polymers. Once chains have diffused by their radius of gyration, the properties of the interface should be indistinguishable from those of the bulk. In practice, welds can achieve bulk strength at much shorter times. The mechanism of strength growth is difficult to determine with experiments, because they cannot directly access the evolution of molecular configurations and entanglements. Large-scale simulations were used to follow the dynamics of interdiffusion at welds and cracks and the associated changes in density and molecular conformations[1]. The evolution of entanglements was tracked using Primitive Path Analysis and shown to be directly related to the mechanical strength under shear and tensile loading. As in experiment, the maximum shear strength  $\sigma_{\max}$  of a homopolymer interface rises as a power of welding time  $t$  and then saturates at the bulk value. Simulations show that  $\sigma_{\max}$  is proportional to the areal density of interfacial entanglements at short times and saturates when chains have formed 2-3 entanglements across the interface. Enthalpy limits interdiffusion across heteropolymer interfaces, and there is a corresponding reduction in interfacial entanglements and mechanical strength. A minimum loop length of order the entanglement length must diffuse across the interface to form entanglements. Cracks are more complicated because of the presence of short segments produced during fracture. Segments that are too short to confer bulk strength, but longer than the entanglement length, remain near the interface for long time intervals. This leads to a plateau in strength that is below the bulk value. Crazes form under tensile loading. A low interfacial entanglement density can stabilize craze formation and significantly enhance the fracture energy, but the bulk fracture energy is recovered at about the same time as bulk shear strength.

Supported by NSF Grant DMR-1006805, CMMI-0923018 and OCI-0963185.

[1] T. Ge, G. S. Grest and M. O. Robbins, ACS Macro Letters 2, 882-886 (2013) T. Ge, F. Pierce, D. Perahia, G. S. Grest and M. O. Robbins, Phys. Rev. Lett. 110, 098301 (2013).

## **Multiscale Analysis of Multilayer Composite Pipes**

Pham Dinh Chi, Sridhar Narayanaswamy

Engineering Mechanics Department, Institute of High Performance Computing  
1 Fusionopolis Way, #16-16 Connexis, Singapore 138632

The use of composite materials in offshore applications has constantly increased towards the development of deepwater technology and ultra-deepwater feasibility. Cylindrical composite pipes are the most principal components in floating and offshore platforms. Composite pipes could be grouped into bonded and unbonded structures. Typical bonded composite structures comprise a core angle ply laminate cylinder sandwiched between an inner liner and an outer liner made of elastomer or metal alloys. On the other hand, unbonded composite pipes such as flexible pipes in floating platforms consist of multiple metallic and polymeric layers, among which tensile wires play essential roles in providing axial and bending stiffnesses. The flexibility in motion of each layers of the unbonded composite pipe and the complexity in their geometries and materials make the analysis of unbonded composite structures very challenging. In this work, multiscale non-linear analyses of unbonded flexible risers are carried out and the non-linear behaviors of individual riser layers as well as stick-slip mechanisms between them are studied. In addition, the work also discusses the potential of flexible fiber-reinforced pipe where metal armour strips may be replaced by fiber-reinforced composite materials to significantly enhance the structural performance of conventional pipe.

## Nucleation barrier to registration of lipid bilayer domains

J. J. Williamson, P. D. Olmsted

Department of Physics, Georgetown University, Washington DC 20057, USA

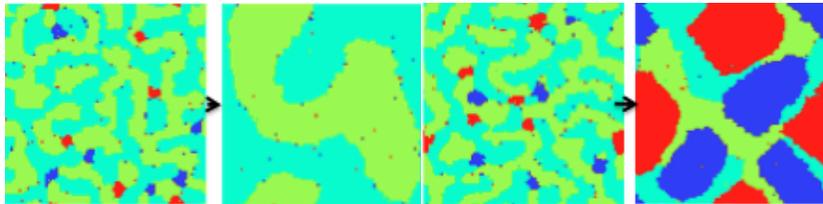
In cellular processes involving lipid bilayer phase separation, equally as important is registration (alignment) of domains between the two leaflets. Most work has focused on measuring or calculating a free energy per area for “direct” inter-leaflet coupling taking place across the midplane [1, 2]. This coupling would favour registration of like domains, as typically seen for macroscopic domains in experiment [3].

However, we show that hydrophobic mismatch between lipid species leads to an additional “indirect” coupling acting to minimise overall thickness variations, favouring *antiregistration*. Thus, domain registration is subject to a competition of two distinct coupling mechanisms.

We use a coarse-grained lattice simulation to show that this renders domain registration a *nucleation-like process*; bilayers may fail to reach their equilibrium, registered state. Given that antiregistration is often unresolvable in experiment, this has important implications for interpreting observed phase behaviour. Crucially, this applies even for a 50:50 mixture of phases, which would naively imply spinodal decomposition. The physics will also bear directly on cellular functions in which inter-leaflet coupling plays a role, e.g. protein signaling [4].

A continuum theory is developed to explain the dependence of nucleation energetics on material parameters. The results show the complex role of lipid length mismatch, and motivate a variety of future work in which the transition between antiregistration and registration is considered.

This work was initiated under the CAPITALS programme grant funded by EPSRC UK.



**Figure 1:** Two trajectories with identical parameters. Registered domains (red/blue) form stochastically via *nucleation*. On the left, this is unsuccessful and the bilayer is metastably trapped out of registration.

[1] S. May, *Soft Matter* 5, 3148 (2009).

[2] H. J. Risselada and S. J. Marrink, *PNAS* 105, 17367 (2008).

[3] J. Korlach, P. Schwille, W. W. Webb, and G. W. Feigen-son, *PNAS* 96, 8461 (1999).

[4] A. Kusumi, I. Koyama-Honda, and K. Suzuki, *Traffic* 5, 213 (2004).

## **Molecular Mechanism of viscoelasticity in aligned polyethylene**

A. Hammad<sup>1</sup>, H. Hasan<sup>1</sup>, T. D. Swinburne<sup>1</sup>, S. Del Rosso<sup>2</sup>, L. Iannucci<sup>2</sup>, A. P. Sutton<sup>1</sup>.

<sup>1</sup>Department of Physics, Imperial College London, London SW7 2AZ.

<sup>2</sup>Department of Aeronautics, Imperial College London SW7 2AZ.

Ultra-High Molecular Weight Polyethylene (UHMWPE) is widely used in industrial applications due to its low density and high tensile strength. Extensive experimental work has been done to determine its mechanical properties, notably its viscoelasticity. However, an understanding of the link between these macroscopic mechanical properties and molecular processes has so far not been achieved. We begin to address this by considering a simple united atom model of polyethylene chains. We demonstrate the nucleation of solitons from chain ends, as one molecular chain is stretched with respect to another, and how load is transferred between chains in disregistry by intermolecular interactions. An analogy is drawn between solitons in UHMWPE and dislocation loops in a 3D crystal, giving a basis for the mechanical behaviour of UHMWPE in terms of the motion of solitons. Although solitons have been invoked to account for dielectric relaxation in crystalline regions of polyethylene, we believe this may be the first time they are discussed in the context of mechanical properties of aligned polyethylene.

## Mesoscale Modeling of the Interfacial Mechanics of Nanocellulose with Glassy Transparent Polymers

Sinan Keten, Luis Ruiz

North Western University, Dept. of Civil & Environmental Engineering and Dept. of Mechanical Engineering 2145 Sheridan Road Tech A133 Evanston IL 60208

This talk will overview a simulation-based approach to enhancing the mechanical properties of novel transparent thin films and nanocomposites by utilizing cellulose – the most abundant and renewable structural biopolymer found on our planet. Cellulose nanocrystals (CNCs) exhibit outstanding mechanical properties exceeding that of Kevlar, serving as reinforcing domains in nature’s toughest hierarchical nanocomposites such as wood. Yet, weak interfaces at the surfaces of CNCs have so far made it impossible to scale these inherent properties to macroscopic systems. A simple analysis on CNC interfaces that accounts for size and geometry effects will be proposed. Our theory and simulations converge on the prediction that the ideal cross-sectional dimensions maximizing the interfacial fracture energy of CNCs must be approximately 5 by 6 nm in dimensions, which intriguingly are very close to the universal dimensions of CNCs found in wood. This study sheds light on a new design principle pertaining to atomically layered nanomaterials that may guide the synthesis of novel nanocomposites. I will conclude with an outlook on how the nascent properties of nanocellulose building blocks could be further utilized in polymers through validated systematic coarse-graining approaches that marry chemical features with mechanical properties.

- [1] B. Sinko, S. Mishra, L. Ruiz, N. Brandis, S. Keten, "The dimensions of biological cellulose nanocrystals maximize fracture strength", *ACS Macro Letters*, 2014, 3, pp 64–69.
- [2] D. Hsu, W. Xia, S. Arturo, S. Keten, "A Universal Systematically Coarse Grained Model for Methacrylate-based Polymers", in submission.
- [3] W. Xia, S. Keten, "Coupled Effects of the Substrate Adhesion and Intermolecular Forces on Polymer Thin Film Glass-Transition Behavior", *Langmuir*, 2013, 29(41), pp. 12730-12736.
- [4] W. Xia, S. Mishra, S. Keten, "Substrate vs. Free Surface: Competing Effects on the Glass Transition of Polymer Thin Films", *Polymer*, 2013, 54(21), pp. 5942–5951.

## **The Microscopic Effect of Filler on Rubber Reinforcement: A Coarse-Grained Molecular Dynamics Study II**

Kentaro Nagaya<sup>1</sup>, Masatoshi Sato<sup>1</sup>, Yosuke Kimura<sup>1</sup>, Katsumi Hagita<sup>2</sup>

<sup>1</sup> Toyota Technical Development Corporation, NORE Sakuradori bldg, 2-28-23, Izumi, Higashi-ku, Nagoya, Aichi, Japan

<sup>2</sup>National Defense Academy of Japan, 1-10-20, Yokosuka, Kanagawa, Japan

It is well known that adding filler particles such as carbon black to cross-linked rubber raises the stiffness, increases the hysteresis loss due to internal friction and causes stress softening in cyclic deformation (referred to as Mullins effect). Mechanisms by which these macroscopic changes occur are areas in active research. One of the key factors in understanding the occurrence of these phenomena is considered to be microscopic filler-rubber interaction.

In this research, we developed a microscopic approach to understand rubber reinforcement using coarse-grained molecular dynamics simulations<sup>[1]</sup>. In our models, we considered two types of filler-rubber interactions exist: one is physical adsorption and the other is chemical bond. In addition, we also considered variation of filler distribution. Fillers are well dispersed or partially aggregate in our models.

We investigated static uniaxial tensile behavior of filled and unfilled rubber models, and found three reinforcement mechanisms. First is the same mechanism predicted by Guth<sup>[2]</sup>, which depends only on the volume content of fillers. We have confirmed this mechanism at small strain region. Second is caused by filler-filler network created by the advantage of chemical bond at large strain. In this region, some polymers linked fillers and were stretched, that is, these polymers generated tension. Last is caused by contact pressure of aggregated fillers at very small strain region. Aggregated fillers push each other in vertical directions against tensile direction (Poisson ration is 0.5). The third mechanism will be discussed in detail.

[1] K. Kremer and G. S. Grest: J. Chem. Phys. 92, 5057 (1990)

[2] E. Guth: J. Appl. Phys. 16, 20 (1945)

## Multiscale strain field measurement in fibrous membrane of connective tissue with photobleaching

M. Coret<sup>1</sup>, C. Jayyosi<sup>2</sup>, K. Bruyère-Garnier<sup>2</sup>

<sup>1</sup> LUNAM Université, GEM, UMR CNRS 6183, École Centrale de Nantes, Université de Nantes, France

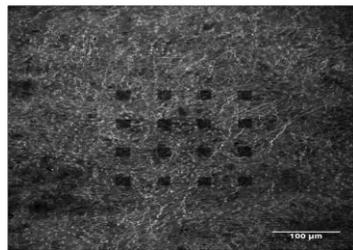
<sup>2</sup> Université de Lyon, F-69622 Lyon ; IFSTTAR, LBMC, UMR-T9406 ; Université Lyon1, France

Multiphoton microscopy, combining two photon excitation fluorescence (TPEF) and second harmonics generation (SHG), has proved itself to be one of the most efficient ways to image collagen and elastin based structures. Indeed, considering elastin autofluorescence and collagen second harmonics generation, fibers' network can easily be seen and distinguished thanks to that microscopy technique. Therefore, it turns to be a valuable tool to study soft biological tissue microstructure, and, if coupled with a loading device, it allows seeing how the fibers' network reacts to mechanical loading. Photobleaching is usually seen as a drawback of multiphoton microscopy, as it corresponds to a loss of fluorescence that undergoes the sample when excited with too much laser intensity or too long exposure time.

In this study, using that loss of fluorescence, intrinsic markers were placed on the structure, designing a pattern of photobleached squares as seen on figure 1.

This grid was then used to compute local strain in human liver's capsule submitted to uniaxial tensile test, following the same approach adopted by Screen and Evans[1]. Local strain was derived from calculated displacements at various steps during loading up to failure, using the finite element method on a 4 nodes element mesh built from the photobleached grid. Observations about the geometry and kinematics of the fibers locally, revealed that this technique is non-destructive, and thus can be used to assess local strain in fibrous structures that contain elastin and collagen fibers [2]. These markers can be used in various ways, in order to help understanding the contribution of microstructure to the macroscopic mechanical behavior of the tissue and to study local phenomenon such as damage and failure mechanisms.

The authors thank the IVTV (ANR-10-EQPX-06-01) team for its help and support.



**Figure 1:** Image of the human liver's capsule with a photobleaching grid before loading

[1] H. R. C. Screen and S. L. Evans, "Measuring Strain Distributions in Tendon using Confocal Microscopy and Finite Elements," *J. Strain Anal. Eng. Des.*, vol. 44, no. 5, pp. 327–335, Jul. 2009.

[2] C. Jayyosi, G. Fargier, M. Coret and K. Bruyère-Garnier, "Photobleaching as tool to measure local strain field in fibrous membranes of connective tissues," *Acta Bio.* Accepted, Feb. 2014

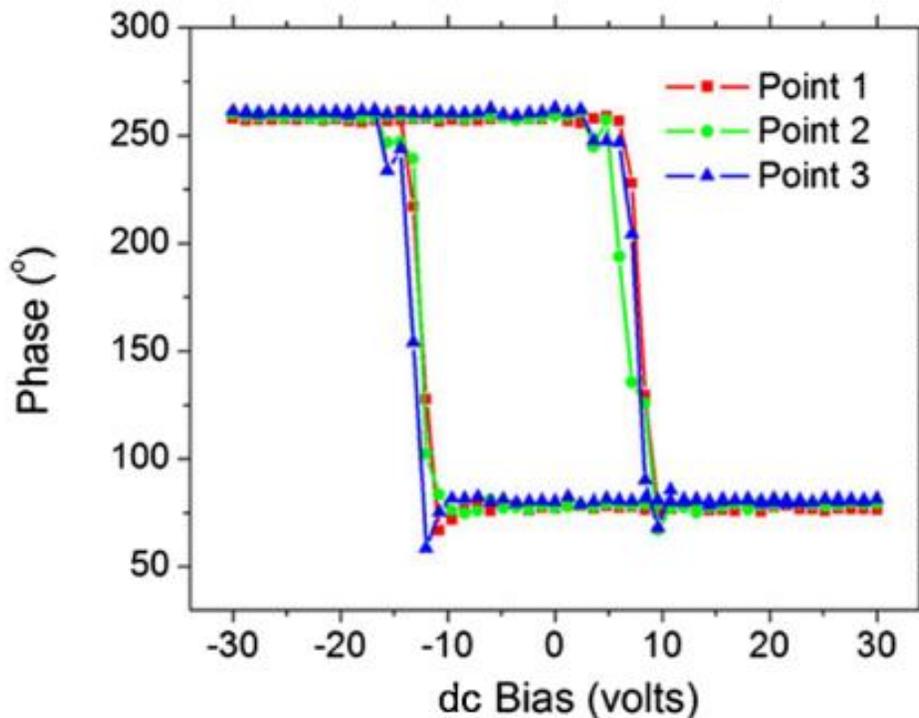
## The Mechanism Underpinning Biological Ferroelectricity

Matthew Zelisko<sup>1</sup>, Jiangyu Li<sup>2</sup>, Pradeep Sharma<sup>1</sup>

<sup>1</sup>Department of Mechanical Engineering, University of Houston, Houston, TX 77204, US

<sup>2</sup>Department of Mechanical Engineering, University of Washington, Seattle, WA 98195, US

Ferroelectricity in biological materials, while speculated, has been a matter of much debate. Recent experimental discovery of this phenomenon in elastin---a key ingredient of aorta, lung, ligament, and skin has given rise to tantalizing questions regarding its origins as well as ramifications. In this presentation, motivated by the experiments performed by one of us, we present a two-scale modeling approach consisting of a coarse-grained statistical mechanics model and molecular dynamics to elucidate the microscopic mechanisms underpinning ferroelectricity in Elastin.



Ferroelectric hysteresis loops of porcine aortic walls observed through PFM<sup>1</sup>

More recent experimental work done by Li *et al.*<sup>2</sup> has shown that the ferroelectric behavior of an elastin network may play an important role in the aging process among other things. As the concentration of glucose in the intercellular elastin matrix increases, similar to what happens as we age, elastin exhibits less of a ferroelectric response, and at high enough glucose concentrations the ferroelectricity of elastin is completely suppressed. Therefore it is hopeful that the statistical mechanics and molecular dynamics

model presented will later be useful in better understanding the aging process in living organisms.

[1] Y. M. Liu, Y. Zhang, M. J. Chow, Q. N. Chen, and J. Li, Phys. Rev. Lett. 108, 078103 (2012).

[2] Y.M. Liu, Y. Wang, M.J. Chow, Q.N. Chen, F. Ma, Y. Zhang, and J. Li. Phys. Rev. Lett. 110, 168101 (2013).