

# **ENABLING CIRCULAR ENGINEERING BY REDESIGNING A DRIVER'S SIDE FRONT DOOR USING ULTRALIGHTWEIGHT THERMOPLASTICS COMPOSITES VIA SYSTEMS LEVEL DESIGN AND SIMULATION STRATEGY**

Srikanth Pilla, Clemson University, USA  
spilla@clemson.edu

Greenhouse gases are one of the primary causes of human induced global warming wherein ~14% of the global greenhouse gas emissions are from the transportation sector. This underscores the vast potential and impact any sustainable paradigm might bring if tailored to the practical realities of the automotive sector. In this context a closed loop multicycle paradigm that goes beyond the reduce, reuse and recycle dogma and emphasizes on the redesigning and remanufacturing of vehicles aka Circular Engineering might just be the solution the automotive sector needs.

A great case for circular engineering can be presented in the context of lightweighting of the automotive structures that would: reduce the weight of the car and material usage, translating to greater fuel efficiency but come coupled with engineering challenges ranging from design to manufacturing. From a materials perspective carbon fiber reinforced thermoplastic composites offer an alluring premise as they provide high stiffness and strength while being lightweight and are recyclable when compared to their thermoset counterparts. However, a major constraint to their immediate adoption include: Understanding their failure behavior in nonlinear crash environments, cost of carbon fiber and cycle time for production.

This work looks into incorporating the principles of circular engineering by delving into the process of designing an ultralightweight thermoplastic composites door (a driver's side front door) and developing robust simulation methods to validate and optimize its crash response. This includes details on the development of robust material cards and their experimental validation at coupon and component level. These robust simulation methods form the cornerstone to rapidly iterate and develop a composite door frame that meets and surpass the crash performance of the baseline metal door.

## GEOLOGIC ENTROPY WITH ECONOMIC CONSTRAINTS PREDICTS MINERAL PRICES

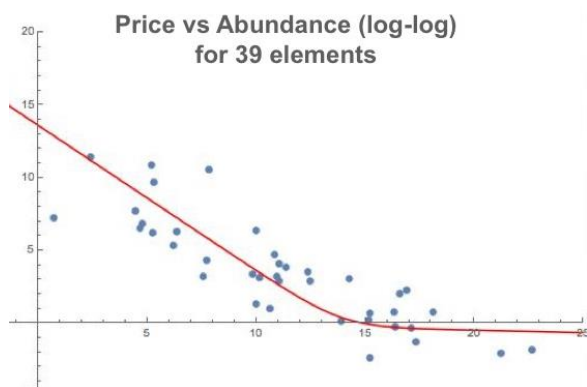
Alan J. Hurd, Los Alamos National Laboratory, USA  
ajhurd@lanl.gov  
Radha Perumal Ramasamy, Anna University

**Key Words:** geologic entropy, price, abundance, sustainability

We propose a geologic entropy for describing the price of an element from its abundance. Maximizing a geologic entropy function under economic constraints using the Lagrange multiplier method yields specific predictions verifiable by data.

By now sustainability theory has established the existential need for managing consumption and closing recycling loops for materials. In 2019, society experienced a serious shortage in helium that substantially impacted the research community. A similar crisis for rare earth materials occurred in 2010. In both cases market factors were important to the supply risk, and new insights into the relation between market price and mineral element availability will presumably be helpful in understanding shortages.

Upon maximizing entropy subject to constraints, our method reproduced the empirical power-law behavior observed between price and abundance. We also investigated models that assume an exponential "activated process" for mining an element and for a highly regulated economy with fixed prices. Results indicate that the most likely abundance distribution under economic constraints yields a price-availability relation that is, within the spread of the data, identical to conventional supply and demand conditions in mineral economics.



*Figure 1 – Analytic theory predicts price-abundance relation for chemical elements based on proposed geologic entropy with economic constraints.*

This work opens a window into a useful entropy function for geology and a way to apply economic constraints in a simple way that could help us better understand the parallels between statistical physics and economics. The underlying principle is that there is a most likely distribution of elemental abundances in a large ensemble of inhabitable planets as a way to define a useful entropy function. (This distribution is NOT claimed to be spatial distribution, which is well beyond our present capability and need, but rather a global average available to inhabitants to run a society.) We apply constraints—such as total expense cap and highly regulated prices—by maximizing the geologic entropy using Lagrange multipliers, thereby providing specific predictions verifiable by data. Surprisingly, results indicate that supply and demand aspects emerge with only statistical predicate. This work opens a window into a useful entropy function for geo-economics and a way to apply economic constraints using statistical physics.

## GEOPOLYMERS: STRUCTURAL INORGANIC POLYMERS AND A POTENTIAL PARTIAL SOLUTION TO GLOBAL WARMING

Waltraud M. Kriven, University of Illinois at Urbana-Champaign, USA  
kriven@illinois.edu

“Geopolymers” are polysialates which are charge-balanced, aluminosilicate, ceramic-like materials made from an aluminosilicate source such as metakaolin, i.e., calcined clay and alkali metasilicate “waterglass” solution. A stoichiometric chemical composition is  $M_2O \cdot Al_2O_3 \cdot 4SiO_2 \cdot 11H_2O$  where M may be Group I element such as Na, K, or Cs and the water content depends on particle size, specific surface area and aluminosilicate source. The inorganic polymer is made by high shear mixing with the liquid suspension undergoing dissolution, polycondensation or precipitation under ambient conditions. The resulting inorganic polymer has a microstructure which is impervious, nanoporous (diameter  $\sim 6.8$  nm), of  $\sim 40$  vol % nanoporosity, and is nanoparticulate (10-40 nm).

The ceramic-like, cross-linked product shares the brittle nature of ceramics, but can be reinforced with particulates, platelets, chopped fibers, uniaxial fibers, or fiber weaves yielding a strong and tough composite, which is fire and acid corrosion resistant. Geopolymer composites reinforced with various biological fibers (hemp, curua, sisal, malva, jute, etc) have been made. In the Amazon the clays under the jungles consist of fine high quality kaolinite clay containing 25 wt % particulate quartz reinforcements. Such geopolymer composites have comparable flexure strengths to high strength concrete, when reinforced with chopped reinforcements of Guadua Angustifolia bamboo. Their mechanical properties, durability and shrinkage behavior were measured to assess their suitability as building construction materials.

Geopolymers also have refractory and adhesive properties up to  $1,000^\circ\text{C}$  whereupon they crystallize into ceramics of tailorable, crystallographic thermal expansion. The CTE's of crystallized geopolymers range from  $\sim 0.45 \times 10^{-6} \text{ }^\circ\text{C}^{-1}$  to  $\sim 50 \times 10^{-6} \text{ }^\circ\text{C}^{-1}$  depending on the compositions and ratios of Cs, K, or Na charge balancing cations. The charge balancing cations lie in pore channels in the [111] unit cell directions. Comparing across temperatures, phases with cubic symmetry exhibit a monotonic decrease in volumetric thermal expansion at all temperatures with increasing cesium content. Comparing across K-Cs compositions, the linearity of each curve increases with increasing cesium content. Only crystalline  $K[AlSi_2O_6]$  and  $K_{0.8}Cs_{0.2}[AlSi_2O_6]$  existed in tetragonal symmetry above RT. In contrast to cubic phases, the tetragonal phases exhibited increasing thermal expansion with temperature. Thermal expansion tensors can give insight into the asymmetry of expansion in this system. From these, it is apparent that the volumetric expansion is due to expansion along the [100] and [010] axes. The cell contracts along the [001] axis contracts and does so more rapidly with increasing temp.

Under inert nitrogen or argon gases at  $1400^\circ\text{C}$  to  $1600^\circ\text{C}$ , nanoparticulate geopolymers with only nano length diffusion distances undergo carbothermal reduction or carbothermal nitridation forming soft agglomerates of SiC,  $Si_3N_4$  or SiAlON nanoparticles. Geopolymers are a potential partial solution to global warming. This is  $\sim 900^\circ\text{C}$  below the formation of SiC via the Acheson process, and requires only minor grinding of the resulting nano SiC agglomerates.

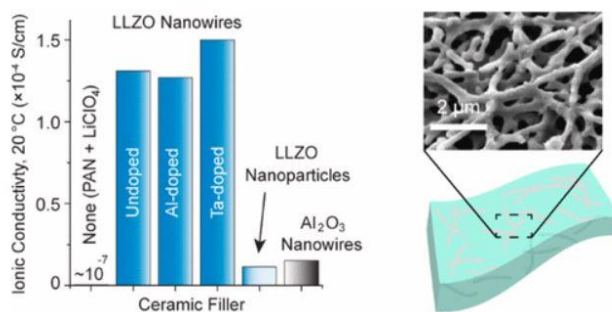
While the term “geopolymers” is used widely in the alkali activated community which uses waste streams of Class F fly ash and slag with sodium hydroxide, our recent studies show that this actually results primarily in the formation of C-N-A-S-H (calcium sodium aluminum silicate hydrate) gel binder phase rather than the stoichiometric geopolymer described above. NASH steadily loses its tensile strength and Young's modulus by  $\sim 700^\circ\text{C}$ .

## COMPOSITE POLYMER ELECTROLYTES FOR ALL-SOLID-STATE LITHIUM BATTERIES USING NANOSTRUCTURED CERAMIC GARNET FILLERS

Candace K. Chan, Arizona State University, USA  
candace.chan@asu.edu

Key Words: Lithium batteries, solid electrolytes, garnet, polymer composite

The Li ion conducting garnet  $\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$  (LLZO) has attracted substantial interest as a solid electrolyte for next generation, all-solid-state lithium batteries on account of its relatively high ionic conductivity of  $\sim 10^{-4} \text{ S cm}^{-1}$ , non-reactivity with lithium, and wide voltage stability window ( $> 5 \text{ V vs. Li/Li}^+$ )<sup>1</sup>. Although more than a decade has passed since LLZO was first reported<sup>2</sup>, the application of LLZO as a ceramic electrolyte in all-solid-state batteries is still met with several practical challenges due to its brittle nature and the difficulty of forming good contacts or interfaces with electrodes<sup>3</sup>. Recently, the incorporation of LLZO as nanostructured ceramic fillers within solid polymer electrolytes has received great interest. The application of nano-sized particles as ceramic fillers has already been demonstrated to be effective for enhancing the mechanical stability and ionic conductivity of polymer-based solid electrolytes, but these fillers have mostly consisted of spherical particles of inert or “passive” components without intrinsic  $\text{Li}^+$  conductivity. Recent studies using LLZO-embedded into polymer films have revealed different degrees of effectiveness, indicating that more careful design of the composite polymer electrolytes (CPEs), including optimization of the LLZO filler properties and more detailed mechanistic study of the  $\text{Li}^+$  transport pathways, may be needed for the development of CPEs with high ionic conductivity. In our work<sup>4</sup>, we show that by incorporating only 5 wt% of electrospun LLZO nanowires into a polyacrylonitrile- $\text{LiClO}_4$  matrix, the room temperature ionic conductivity of the composite is increased 3 orders of magnitude to  $1.31 \times 10^{-4} \text{ S/cm}$ . CPEs made using LLZO nanoparticle and  $\text{Al}_2\text{O}_3$  nanowire fillers are also studied to elucidate the role of filler type (active vs. passive), LLZO composition (undoped vs. doped), and morphology (nanowire vs. nanoparticle) on the CPE conductivity. It is demonstrated that both intrinsic  $\text{Li}^+$  conductivity and nanowire morphology are needed for optimum performance. Subsequent studies using solid-state nuclear magnetic resonance and synchrotron X-ray fluorescence microscopy are used to investigate the Li transport pathways and understand the dispersion of the nanowires within the composite films.



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4. T. Yang, J. Zheng, Q. Cheng, Y.Y. Hu, C.K. Chan, Composite polymer electrolytes with  $\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$  garnet-type nanowires as ceramic fillers: mechanism of conductivity enhancement and role of doping and morphology, *ACS Appl. Mater. Interfaces*, 9 (2017) 21773 – 21780.

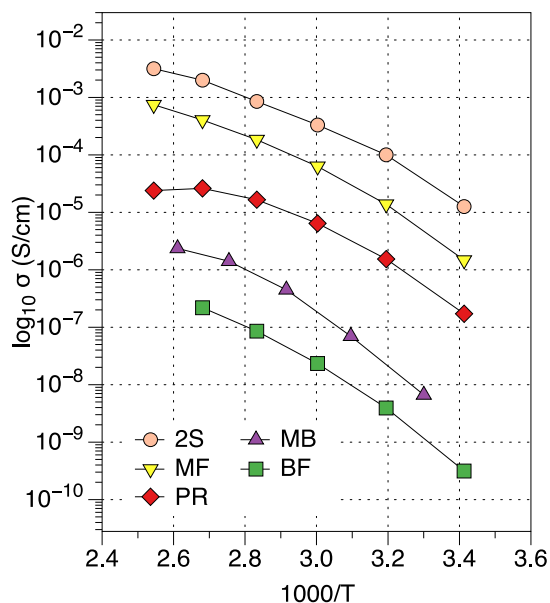
# HYBRID ORGANIC-INORGANIC NANO-COMPOSITES FOR SOLID-STATE BATTERY ELECTROLYTES

John Kieffer, University of Michigan, USA  
 kieffer@umich.edu  
 Vazrik Keshishian, University of Michigan, USA  
 Cameran Beg, University of Michigan, USA  
 Weimin Wang, University of Michigan, USA

**Key Words:** battery electrolytes, hybrid materials, transition state theory, molecular dynamics.

Desired properties of solid electrolytes are high ionic conductivity and transference number, high shear modulus to prevent dendrite growth, chemical compatibility with electrodes, and ease of fabrication into thin films. Especially, elastic stiffness and ionic mobility are opposing attributes in a homogenous material, and a composite approach towards designing novel electrolytes is therefore advisable. We use a two-step sol-gel method to synthesize silica-based hybrid organic-inorganic materials for this application. First, a continuous porous silica structure is created that provides electrochemical stability and mechanical rigidity. This network also contains unreacted epoxy groups. In step 2, single-sided amine-functionalized polyethene glycol (PEG-NH<sub>2</sub>) infiltrates the pores via fluid exchange. As PEG-NH<sub>2</sub> fills the pores, the amine groups react with the epoxy groups and anchor the polymer to the silica network, which provides highly conductive pathways. IR spectroscopy, Raman and Brillouin light scattering, impedance spectroscopy, small angle x-ray scattering

(SAXS), charge-discharge cell testing is performed to identify the structural and chemical origins that underlie the performance of these hybrid electrolytes. A room temperature ionic conductivity in excess of 10<sup>-5</sup> S/cm is reached (Fig. 1).



**Fig. 1** Conductivity as a function of temperature for: (MB) silica xerogel mechanically blended with PEG, (BF) bi-functional PEG (reactive on both ends) co-polymerized with silica, (PR) bi-functional PEG partially co-polymerized with silica, (MF) mono-functional PEG co-polymerized with silica, and (2S) mono-functional PEG grafted on silica in a two-step process.

The covalent bonding between polymer and silica is essential to enhancing the ionic conductivity without sacrificing mechanical stability. To better understand the reason for this we conducted systematic investigations into the mechanisms of cation transport in amorphous structures, both experimental and computational. We found that, for mixed network former glasses, the adiabatic bulk elastic modulus, measured using Brillouin light scattering (BLS), and the activation energy for the modifier cation conductivity are strictly correlated. Using data from NMR spectroscopy and BLS as input for a reaction equilibrium-based statistical thermodynamic analysis we derived a quantitative account of all possible network building units. The resulting statistical measures for the distribution of cation hopping pathways in these glasses led to the development of an improved transition state theory model for ion conduction in these materials [1]. Our model allows us to assess the spatial extent of this deformation, as well as estimate the relative amounts of configurational and vibrational entropy changes associated with this thermally activated process. Atomistic models of these glasses established using MD simulations based on a reactive force field further substantiate our new kinetic theory, and allow us to derive materials design criteria for materials with simultaneously high ionic conductivity and elastic moduli.

Acknowledgement: NSF-DMR 1610742

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# UNDERSTANDING THE EVOLUTION OF THE SILICON ELECTRODE SEI THROUGH MODEL LITHIUM SILICATE THIN FILM LAYERS

Christopher Apblett, Sandia National Laboratories, USA  
caapble@sandia.gov

Jaclyn Coyle, National Renewable Energy Laboratory

Gabriel Veith, Oak Ridge National Laboratory

Michael Brumbach, Sandia National Laboratory, USA

Key Words: Silicon, Anode, Electrochemistry, SEI, Silicates.

Development of higher capacity anodes in lithium ion batteries for use in electric vehicles is necessary to further enhance their energy density. Silicon anodes are being considered for these lithium ion batteries due to their high specific capacity. One drawback to silicon anodes is the formation of an unstable solid electrolyte interface (SEI). A major cause of this instability is due to silicon anode volume expansion of up to 300% during cycling. To this end, there remains much to learn about the chemical reactions occurring at the silicon surface. Because of this expansion, composite Si-graphite electrodes exhibit poor cycling performance, as well as significant capacity loss even at open circuit, "shelf" conditions in the absence of electrochemical cycling. Implicated in these processes is the role of the solid/electrolyte interphase (SEI) region between the Si solid material and the electrolyte systems that forms upon initial exposure to the electrolyte, and evolves over time. Thermodynamic arguments suggest that the formation of lithium silicate ( $\text{LiSi}_x\text{O}_y$ ) phases from the decomposition of the electrolyte at the silicon electrochemical potential play a role in SEI formation and evolution. To better understand the evolution of the SEI layer and the nature of silicates formed prior to any cycling of the silicon anode and how it impacts the performance of the silicon anode, model SEI layers were deposited on silicon thin films using RF magnetron co-sputtering. Thin film chemistries from  $\text{SiO}_2$  to  $\text{Li}_3\text{SiO}_x$  were synthesized to model the proposed lithiation of the oxide layer during the first cycle. The composition and structure of these thin films prior to exposure to electrolyte were analyzed. In order to observe the chemical reactivity of these model silicate thin films, they were soaked in 1.2M  $\text{LiPF}_6$  in EC:EMC 3:7 wt% electrolyte for up to 3 days, removed, rinsed and studied using Attenuated Total Reflectance Infrared Spectroscopy (ATR IR), X-ray Photoelectron spectroscopy (XPS) and Focused Ion Beam Cross-sections (FIB CS). Half cells with these same silicate model films were cycled to observe any differences in SEI formation or cell performance during electrochemical cycling.

Results on these model films after soaking in the electrolyte indicate a dependence on stoichiometry for surface reactivity over time. For low order silicates the composition and thickness are unchanged, but as the lithium content in the film increases, increasing fluorine content is observed through the film, along with reductions in thickness, indicating attack of the film by the electrolyte or its byproducts. It is theorized that this increased reaction rate is a function of the amount of non-bridging oxygens terminated by lithium metal ions in the silicate film. From electrochemical measurements, the presence of lithiated silicates at the surface of the silicon anode affects the kinetics of the initial lithiation of the silicon anode as well as the stability of the cell with continued cycling. These model systems have started to tease apart the complexity of the surface reactivity and lithiation kinetics that manifest during storage and cycling of silicon anodes.

Sandia National Laboratories is a multimission laboratory managed and operated by National Technology & Engineering Solutions of Sandia, LLC, a wholly owned subsidiary of Honeywell International Inc., for the U.S. Department of Energy's National Nuclear Security Administration under contract DE-NA0003525.

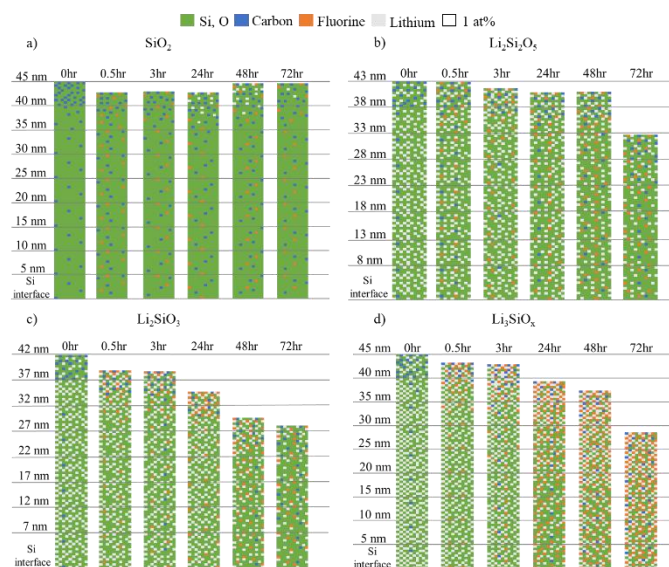


Figure 2 Illustration of thickness and compositional changes of a)  $\text{SiO}_2$ , b)  $\text{Li}_2\text{Si}_2\text{O}_5$ , c)  $\text{Li}_2\text{SiO}_3$ , and d)  $\text{Li}_3\text{SiO}_x$  films exposed to electrolyte over time.



## DENSE CERAMIC CATHODES FOR LITHIUM AND SODIUM BATTERIES

Paul Braun, University of Illinois at Urbana-Champaign, USA  
pbraun@illinois.edu

Key Words:  $\text{LiCoO}_2$ , Li-ion batteries, high energy density, electrodeposition

Electrodeposition of dense ceramic electrode materials has the potential to enhance secondary battery performance and mechanics, and broaden the scope of available electrode form factors. I will present our work on the electrodeposition of high performance  $\text{LiCoO}_2$ ,  $\text{NaCoO}_2$ ,  $\text{LiMn}_2\text{O}_4$ , and Al-doped  $\text{LiCoO}_2$ -based Na and Li-ion cathodes as well as related materials. The electrolytically active materials were formed as solid films, with densities as high as 95%, and in thicknesses as great as 200  $\mu\text{m}$ . The capacities are near-theoretical and the crystallinities and electrochemical capacities are comparable to powders synthesized at much higher temperatures. By using electrodeposition to grow the materials, the growth temperature was reduced from 700-1000  $^\circ\text{C}$ , the typical temperature for the solid-state synthesis of most cathode materials to 200-300  $^\circ\text{C}$ , which both enabled the direct growth of the nearly solid cathode on a metal current collector, and reduces the overall energy input required to grow the cathodes. We also find the electrodeposited films can be high textured, and in some cases, the crystals can be oriented such that the fast ion and electron diffusion pathways are normal to the substrate, which results in electrodes with unexpectedly good rate performances.

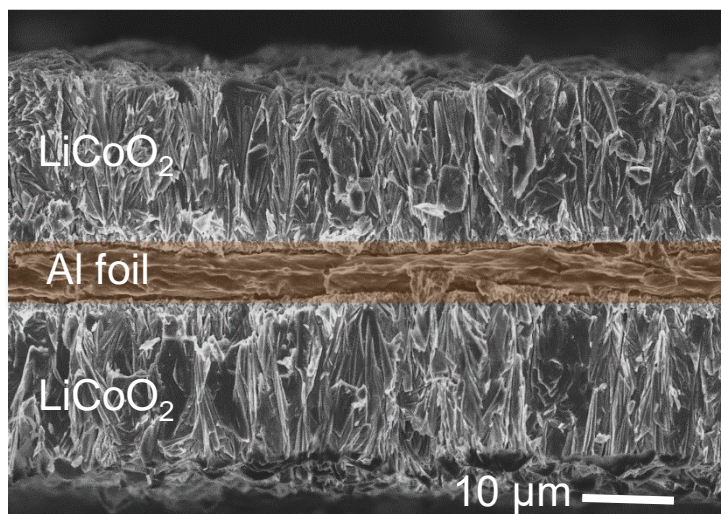


Figure 3 –  $\text{LiCoO}_2$  electrodeposited on both sides of an aluminum current collector.

Figure 1 shows  $\text{LiCoO}_2$  layers on both sides of an Al foil current collector. The  $\text{LiCoO}_2$  was formed via electrodeposition in a molten salt and could be grown with a porosity as small as 5%. The appearance of the other solid cathodes formed via electrodeposition is similar. Because there is no binder or conductive additive, the energy density of the electrodeposited layer is greater than that of a conventional electrode, and because it is nearly dense and binder-free, the electrodeposited film also serves to enhance the mechanical properties of the Al film.

## SELF-HEALING COPOLYMERS via VAN DER WAALS INTERACTIONS

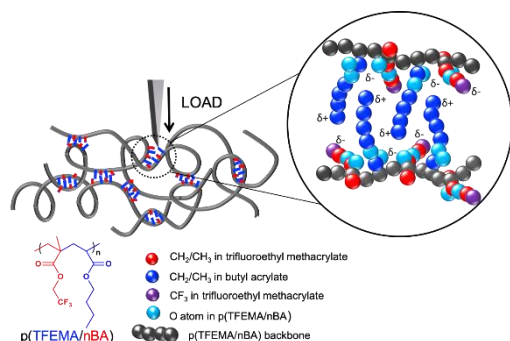
Marek W. Urban, Clemson University, Dept. Mater. Science and Eng., USA.

mareku@clemson.edu

Siyang Wang, Clemson University, Dept. Mater. Science and Eng., USA.

Key Words: Self-Healing Copolymers

Materials with build-in responsive components are outstanding candidates for the development of sustainable technologies. Last decade efforts have primarily focused in incorporating supramolecular chemistry and reversible covalent bonding in the development of self-healing polymers. This lecture will outline recent advances in self-healing polymers, with the primary focus on the recent advances in the development of commodity self-healable polymers. Inspired by plants, self-healing can be achieved by incorporating viscoelastic responses to their microstructures during their formation, thus enabling deformation upon mechanical damage to close a wound. This can be achieved by introducing multiphase-separated polymers composed of polycaprolactone, butanediol, and hexamethylene diisocyanate precursors copolymerized into a self-healing polymer.(1) The presence of micro-phase separated fibrous morphologies facilitate repeatable self-healing due to stable interfacial regions between the hard and soft segments of the copolymer, thus enabling of storage of



entropic energy upon mechanical damage to be recovered during self-healing. This talk will provide the framework of van der Waals interactions in acrylic-based copolymers able to self-heal upon mechanical damage.(2) This behavior occurs when the monomer molar ratios are within a relatively narrow compositional range, forming reversible 'key-and-lock' interactions with preferentially alternating copolymer topologies. The unique self-healing behavior is attributed to favorable inter-chain van der Waals (vdW) forces manifested by the increased cohesive energy densities (CED) forming 'key-and-lock' inter-chain junctions, enabling multiple recovery upon mechanical damage without external intervention.

The concept of redesigning commodity copolymers without elaborate chemical modifications will facilitate a platform for many technological opportunities and the development of new generations of sustainable copolymers with controlled chain topologies that survive repetitive damage-repair cycles.

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2. Science, 2018, 362 (6411), 220-225.



# VAPOR PHASE INFILTRATION FOR TRANSFORMING POLYMERS INTO ORGANIC-INORGANIC HYBRID MATERIALS: PROCESSING SCIENCE, STRUCTURAL COMPLEXITY, AND EMERGING APPLICATIONS

Mark D. Losego, School of Materials Science and Engineering, Georgia Tech, USA  
losego@gatech.edu

Emily McGuinness, School of Materials Science and Engineering, Georgia Tech, USA

Collen Leng, School of Materials Science and Engineering, Georgia Tech, USA

Fengyi Zhang, School of Chemical and Biomolecular Engineering, Georgia Tech, USA

Ryan Lively, School of Chemical and Biomolecular Engineering, Georgia Tech, USA

**Key Words:** Hybrid Materials, Vapor Phase Processing, Kinetics, Membranes, Atomic Layer Deposition

Vapor phase infiltration (VPI) exposes polymers to gaseous metalorganic molecules that sorb, diffuse, and become entrapped in the bulk polymer, transforming it into a complex organic-inorganic hybrid material.<sup>1</sup> This process is pictured in Figure 1. While VPI's gaseous dosing sequences may appear similar to other vapor deposition techniques (e.g., atomic layer deposition) the set of atomic scale processes occurring during synthesis constitute a fundamentally different process that results in not just a simple coating on the polymer but rather a complete alteration of the polymer's bulk chemistry.

This talk will discuss our development of a thermodynamic and kinetics framework for understanding the VPI materials synthesis process<sup>2</sup> and how different mechanisms of entrapment can create either three-dimensionally, covalently bonded organic-inorganic networks or, perhaps more interesting, segregated organic and inorganic networks that interpenetrate at the atomic scale but do not form primary bonds with each other. These unusual structures challenge our definition of concepts like “phases” and “interfaces” that we typically use to describe the physiochemical structure of most materials. In this talk, we will ask the audience to consider if the language we use to classify hybrid materials and nanocomposites is appropriate and sufficient.

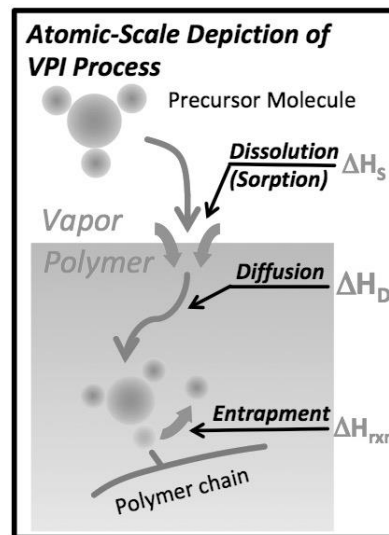


Figure 1 – Depiction of the atomic scale processes important in VPI.

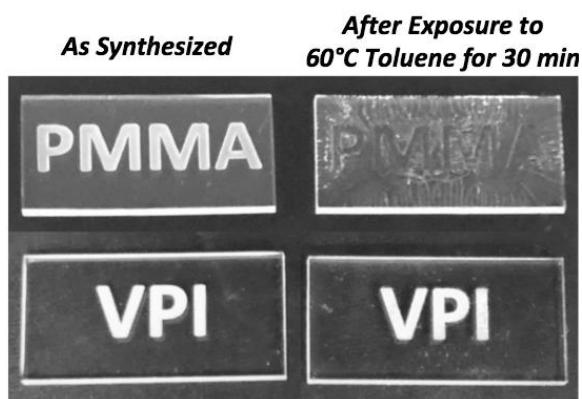


Figure 2 – Photographs of PMMA and VPI treated PMMA (1 exposure cycle to trimethyl - aluminum and water) before and after exposure to hot toluene for 30 min.

This atomic scale intermixing of organic and inorganic constituents generates new physiochemical properties in the material, including a resistance to dissolution or swelling in organic solvents. In certain cases, it is sufficient to infiltrate just a few microns into the subsurface of a polymer to protect the entire polymer (See Figure 2). In other cases, like membranes, we transform the entire material so that it can operate in otherwise “extreme” conditions with little change in performance. Interestingly, the swelling and dissolution behaviors of hybrids with bound and unbound organic-inorganic constituents can vary and appear to depend more upon this bonding environment than the inorganic loading fraction. Perhaps most importantly, many of these modifications can be accomplished with a single exposure to the metalorganic vapors, implying the process can be readily scaled for manufacturing.

<sup>1</sup> C. Z. Leng, M. D. Losego, “Vapor phase infiltration (VPI) for transforming polymers into organic-inorganic hybrid materials: a critical review of current progress and future challenges.” *Mater. Horiz.* 4 747 (2017).

<sup>2</sup> C. Z. Leng, M. D. Losego, “A physiochemical processing kinetics model for the vapor phase infiltration of polymers: measuring the energetics of precursor-polymer sorption, diffusion, and reaction.” *Phys. Chem. Chem. Phys.* 20 21506 (2018).

## NEW FURAN-BASED THERMOSETTING POLYMER SYSTEMS

Giuseppe R. Palmese, Department of Chemical and Biological Engineering, Drexel University, USA  
grp27@drexel.edu

Key Words: furan, epoxy, benzoxazine, mechanical properties, bio-based

Furan building blocks for chemicals and polymers are derived from the processing of cellulose and hemicellulose. A new family of furan-based thermosetting materials will be discussed. Furfuryl amine (FA) was coupled using aldehydes and di-aldehydes to form di-furan di-amine (DFDA) and terra-furan tetra-amine (TFTA) molecules containing two or four furan rings respectively (Figure 1). These amines form the basis for epoxy, benzoxazine, and polyimide thermosetting systems with unique properties (Figure 2). Furan-based epoxy amine systems were found to possess higher density and Young's modulus (>5 GPa), as well as higher yield strength (>150 MPa in compression) and high char-yield compared to traditional epoxies. Benzoxazine monomers were synthesized by reacting DFDA's with a number of phenolic compounds and formaldehyde resulting in solid powders that melt at temperatures ranging between 70°C and 150°C to form low-viscosity liquids. Onset cure temperature varied in the range of 120°C-240°C depending on composition. The resulting polybenzoxazine systems possess Tg's ranging from 220°C to 280°C and char-yield as high as 70% measured at 800°C by TGA in an inert environment. DFDA was also used to prepare nadic end-capped polyimides analogous to PMR-15. These materials were found to process high Tg (>330°C) and excellent processing characteristics because of low melt viscosity and facile imidization. This family of thermosetting systems could provide additional capability for composite, coating, and adhesive applications that require good ambient performance characteristics as well as good thermal management in extreme environments.

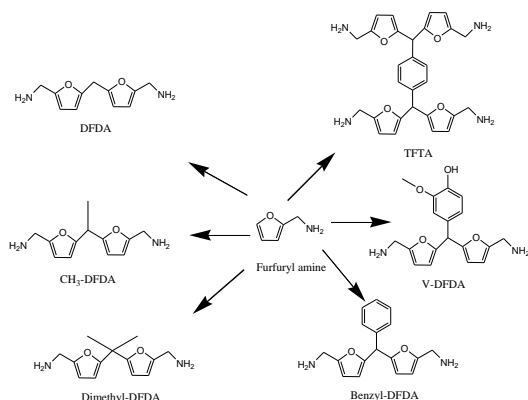


Figure 4 – Di- and tetra-amines obtained from the coupling of furfuryl amine with appropriate aldehydes.

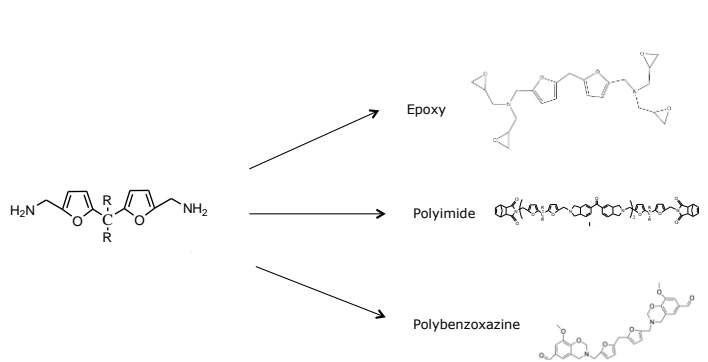


Figure 2 – Use of DFDA type amines as a basis for epoxy, benzoxazine, and polyimide thermosetting systems.

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3. Baroncini E.A., Yadav S.K., Palmese G.R., Stanzione J.F.; Recent advances in bio-based epoxy resins and bio-based epoxy curing agents, *J. Appl. Polym. Sci.* 2016, 133 (45)

## A NEW PARADIGM IN FUNCTIONALLY GRADED ADHESIVES

Daniel Schmidt, UMass Lowell Plastics Engineering / Luxembourg Institute of Science & Technology, USA  
Daniel\_Schmidt@uml.edu

Weiqing Xia, UMass Lowell Plastics Engineering, USA

Sara Najafian, UMass Lowell Mechanical Engineering, USA

Alessandro Cassano, UMass Lowell Mechanical Engineering, USA

Scott Stapleton, UMass Lowell Mechanical Engineering, USA

**Key Words:** functionally graded adhesives, radiation curing

To fully realize the benefits of advanced composites, mechanical fasteners must be supplanted by more efficient technologies such as adhesive bonding. The promise of functionally graded adhesives to provide particularly high levels of performance in this context has been recognized for decades, but a means of generating stable, high performance adhesive joints with arbitrary gradations in mechanical properties has proved elusive.

We report on a new means of realizing such materials in practice, with a focus on the generation of high performance epoxy thermosets with arbitrary gradations. This is accomplished via the creation of so-called “dual cure” resins that may be crosslinked thermally in order to stabilize the joint and realize a baseline level of performance, then selectively irradiated to locally alter levels of crosslinking and performing and induce arbitrary gradations in properties as a result (Figure 1).

A number of different families of dual cure resins have been explored and are introduced here, as well as data concerning changes in thermal and mechanical performance as a function of the details of the dual curing process. Preliminary efforts giving evidence of the generation of stable functional gradations in practice are also described. Ongoing and future efforts are focused on the optimization of these systems and the incorporation of their cure-dependent mechanical behavior into simulations in order to select appropriate designs for functionally graded adhesive joints.

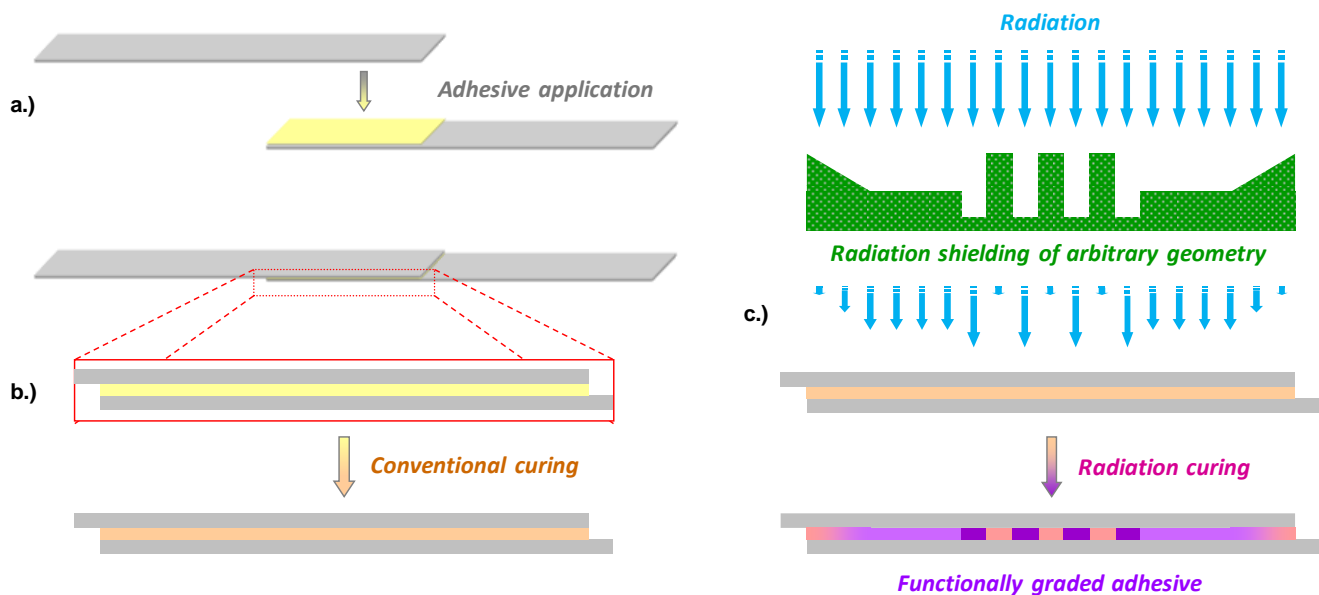


Figure 5 – The “dual cure” concept developed for the generation of stable functionally graded adhesive joints

# NOVEL CALCIUM ION CONDUCTING SOLID ELECTROLYTE WITH NASICON-TYPE STRUCTURE

Nobuhito Imanaka, Osaka University, Japan  
 imanaka@chem.eng.osaka-u.ac.jp

Key Words: Calcium ion, Solid Electrolyte, NASICON-type Structure

Divalent calcium ion conducting solid electrolyte with a three dimensional NASICON-type structure,  $(\text{Ca}_x\text{Hf}_{1-x})_{4/(4-2x)}\text{Nb}(\text{PO}_4)_3$ , was successfully prepared by introducing  $\text{Ca}^{2+}$  cations into the  $\text{HfNb}(\text{PO}_4)_3$  solid. The existence of three kinds of high valence cation of  $\text{Hf}^{4+}$ ,  $\text{Nb}^{5+}$ , and  $\text{P}^{5+}$  successfully realized the effective reduction of electrostatic interaction toward  $\text{Ca}^{2+}$  in the structure. The  $(\text{Ca}_{0.05}\text{Hf}_{0.95})_{4/3.9}\text{Nb}(\text{PO}_4)_3$  solid possesses considerably higher  $\text{Ca}^{2+}$  cation conductivity and also lower activation energy compared with those of previously reported NASICON-type  $\text{Ca}_{0.5}\text{Zr}_2(\text{PO}_4)_3$  solid.

Figure 1 shows the compositional dependence of the lattice volume of the NASICON-type phase estimated by the lattice parameters. By doping  $\text{Ca}^{2+}$  ions into the Hf site in the structure, the lattice volume of the NASICON-type phase monotonously increased with  $x$  up to 0.05 due to the larger ionic size of  $\text{Ca}^{2+}$  (ionic radius:  $0.114 \text{ nm}^3$ ) compared with that of  $\text{Hf}^{4+}$  (ionic radius:  $0.085 \text{ nm}^3$ ), whereas those for the solids with  $x \geq 0.05$  were kept almost constant. These results clearly suggest that the solid solubility limit of the single phase of NASICON-type  $(\text{Ca}_x\text{Hf}_{1-x})_{4/(4-2x)}\text{Nb}(\text{PO}_4)_3$  is approximately  $x = 0.05$ . On the other hand, the conductivity monotonously enhanced with the Ca content until the solid solution limit of  $x = 0.05$  (See Fig. 1).

Figure 2 presents the temperature dependence of the  $\text{Ca}^{2+}$  ion conductivity for  $(\text{Ca}_{0.05}\text{Hf}_{0.95})_{4/3.9}\text{Nb}(\text{PO}_4)_3$  with the corresponding data for the NASICON-type  $\text{Ca}_{0.5}\text{Zr}_2(\text{PO}_4)_3$ . The conductivity of the  $(\text{Ca}_{0.05}\text{Hf}_{0.95})_{4/3.9}\text{Nb}(\text{PO}_4)_3$  solid was appreciably higher than that of the  $\text{Ca}_{0.5}\text{Zr}_2(\text{PO}_4)_3$  solid in the temperature range measured.

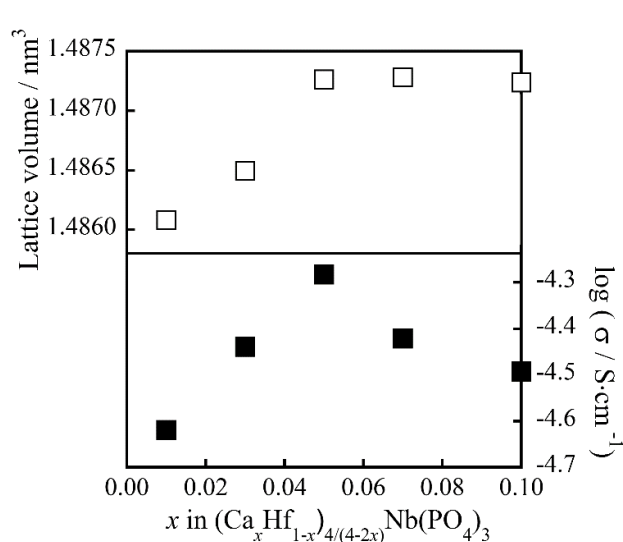


Figure 1 – Compositional dependencies of the lattice volume ( $\square$ ) and the ac conductivity ( $\blacksquare$ ) at 600 °C in air for  $(\text{Ca}_x\text{Hf}_{1-x})_{4/(4-2x)}\text{Nb}(\text{PO}_4)_3$  ( $x = 0.01$ -0.10).

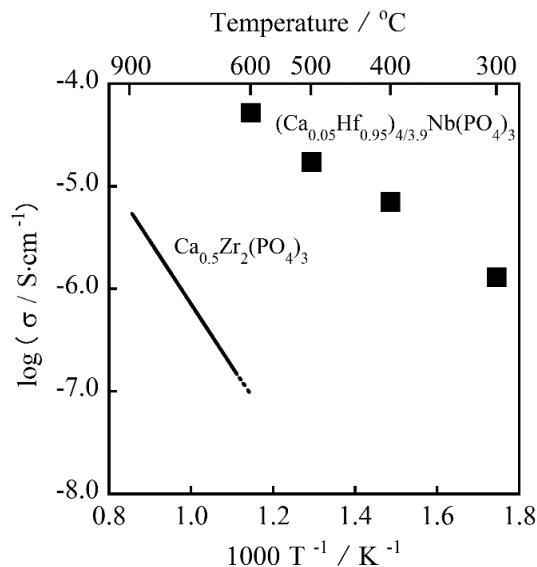


Figure 2 – The temperature dependencies on the ionic conductivity for  $(\text{Ca}_{0.05}\text{Hf}_{0.95})_{4/3.9}\text{Nb}(\text{PO}_4)_3$  ( $\blacksquare$ ) and  $\text{Ca}_{0.5}\text{Zr}_2(\text{PO}_4)_3$  (—).

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## THE ION SEEPS TONIGHT: ASSESSING IONIC TRANSPORT IN MULTILAYERED NANOCOMPOSITES

Erik D. Spoerke, Sandia National Laboratories, USA  
edspoer@sandia.gov

Amanda S. Peretti, Sandia National Laboratories, USA

Stephen J. Percival, Sandia National Laboratories, USA

Leo J. Small, Sandia National Laboratories, USA

Martha M. Gross, Sandia National Laboratories, USA

Eric J. Schindelholz, Sandia National Laboratories, USA

Michael Melia, Sandia National Laboratories, USA

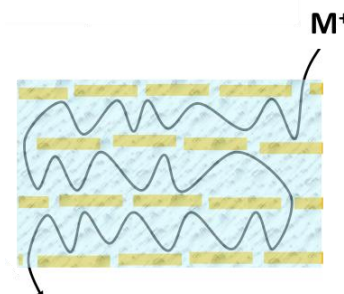
Susan Rempe, Sandia National Laboratories, USA

Derek Nelson, Sandia National Laboratories, USA

Sara Russo, Sandia National Laboratories, USA

**Key Words:** Multilayer Thin Film, Polymer Clay Nanocomposites, Corrosion, Ionic Conductivity, Ionic Selectivity

Controlling ion transport across membranes and interfaces is one of the central themes challenging technological pursuits ranging from corrosion to energy storage and chemical separations. Here, we present several examples in which we have studied the application of multilayer nanocomposites to regulate ion transport. These composites comprise organized layers of functional or structural elements, integrated within composites such that the specific nanostructure and composition of the materials play important roles in defining ionic interactions and mobility. In cases such as corrosion inhibition, thin film composite coatings are intended to block ionic transport, retarding deleterious corrosion reactions. We show that by manipulating the materials chemistry of highly organized polymer clay nanocomposite thin film barriers, it is possible to significantly increase corrosion resistance of steel samples in a simulated sea water environment. In contrast, for energy storage applications such as batteries, composite separators capable of rapid ionic diffusion are desired for high current performance. We explore how layered composite structures may provide effective ion diffusion planes, leading to promising ionic conductivity in new solid state separators. Finally, in chemical separations, the selective transport of ions becomes important. We examine how manipulating the chemical and electrostatic composition of layered polyelectrolyte materials leads to preferential cation transport through these composite structures, a key property for an effective separations membrane. These different technologies exemplify how the principles governing ion transport through multilayered materials can be adapted for widely varied applications, and they illustrate the potential for this materials development strategy to enable new classes of functional composite materials.



*Figure 6 – Schematic of cation ( $M^+$ ) transport through an organized multilayered composite.*

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## **ELECTROCHEMICAL ARTIFICIAL MUSCLE YARNS AND TEXTILES THAT HARVEST AND STORE ENVIRONMENTALLY AVAILABLE ENERGIES**

Ray H. Baughman, Alan G. MacDiarmid NanoTech Institute, University of Texas at Dallas, Richardson, USA  
ray.baughman@utdallas.edu

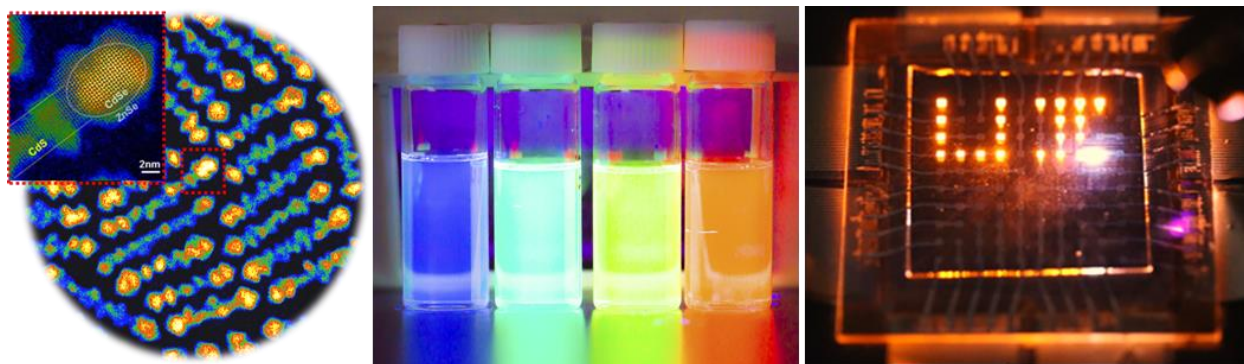
Mechanical energy harvesters are needed for such diverse applications as self-powered wireless sensors, structural and human health monitoring systems, and cheaply harvesting energy from ocean waves. The here reported nanofiber yarn harvesters can electrochemically convert tensile or torsional mechanical energy into electrical energy. Stretching coiled yarns generated 250 W/kg of peak electrical power when cycled up to 30 Hz, and up to 41.2 J/kg of electrical energy per mechanical cycle, when normalized to the weight of the harvester yarn. Unlike for other harvesters, torsional rotation produces both tensile and torsional energy harvesting and no bias voltage is required, even when electrochemically operating in salt water. Since homochiral and heterochiral coiled harvester yarns provide oppositely directed potential changes when stretched, both contribute to output power in a dual-electrode yarn. These energy harvesters were used in the ocean to harvest wave energy, combined with thermally-driven artificial muscles to convert temperature fluctuations to electrical energy, sewn into textiles for use as self-powered respiration sensors, and used to power a LED and to charge a storage capacitor. The development of “piezoelectrochemical spectroscopy” and insights into the hierarchical origins of capacitance increased fundamental understanding. When run in the reverse direction, these muscle types can provide powerful artificial muscles, and the same fibers used as harvesters and muscles can be used to store electrical energy. This work is collaborative with researchers at Hanyang University, University of Texas at Dallas, Lintec of America; Jiangnan Graphene Research Institute, Virginia Tech, and the Wright-Patterson Air Force Research Laboratory.

## MULTI-COMPONENT COLLOIDAL NANOROD HETEROSTRUCTURES AND THEIR OPTOELECTRONIC/PHOTOVOLTAIC APPLICATIONS

Moonsub Shim, Department of Materials Science & Engineering, University of Illinois, USA  
mshim@illinois.edu

Key Words: Colloidal nanorods, quantum dots, LEDs, photovoltaics, multifunctional.

The ability to efficiently separate, recombine, and direct charge carriers is central to a wide range of applications, including electronics, photovoltaics, displays and solid-state lighting. Engineering band structure and heterointerfaces with atomic precision is an obvious route to achieving such capabilities. To do so through widely-accessible and cost-effective means is not. But such a means would allow rapid advances in these critical application areas. The evolution of colloidal semiconductor nanocrystals from single-composition, “spherical” particles to complex heterostructures of diverse shapes provides many opportunities for precision band structure engineering through scalable solution synthesis. With anisotropic shapes that can be exploited for assembly, charge carrier manipulation and optical anisotropy, incorporating heterojunctions and other functional interfaces into colloidal nanorod heterostructures represents an especially promising direction. In this talk, general challenges to the synthesis of complex-yet-well-defined colloidal nanorod heterostructures will first be discussed. Approaches such as spatially selective solution epitaxy, catalytic growth, cation exchange and combinations thereof can be exploited to achieve unique heterostructures with useful properties. A specific example of double-heterojunction nanorods (DHNRs) will be highlighted. Their engineered band structure with shape anisotropy improves charge injection, enhances light outcoupling and increases device lifetime of their light-emitting diodes (LEDs). At the same time, these features of DHNRs facilitate photo-induced charge separation, leading to useful photovoltaic response in high-performance, solution-processed LEDs. Emerging anisotropic colloidal heterostructures such as DHNRs can not only radically improve existing function but also impart new capabilities that could open up new directions for future generations of devices without adding complexity in manufacturing.



*Figure 7 – (From left to right) Transmission electron micrograph of Double Heterojunction Nanorods (DHNRs). Solutions of DHNRs under UV illumination. An array of light-responsive LED pixels incorporating DHNRs. Each pixel is programmed to light up when it detects the laser pointer shining on it.*

## **DIRECT-WRITE ADDITIVE MANUFACTURING OF POLYMER AND CERAMIC COMPOSITES**

Brett Compton, University of Tennessee, USA  
bcompto1@utk.edu

Key Words: polymer, 3D-printing, fiber, orientation, anisotropy

Extrusion-based additive manufacturing (AM) technologies – including fused filament fabrication (FFF) and direct ink writing (DIW) – present opportunities to create composite materials and multi-material architectures that cannot be made using other AM technologies. The direct deposition nature of these processes enable the straightforward deposition of multiple materials through the use of multiple print heads, while the extrusion process preferentially aligns high aspect ratio filler materials like fibers, whiskers, and platelets. This alignment, coupled with the flexibility to choose the print path for each layer provides the ability to prescribe unique fiber arrangements within printed parts.

This talk will focus on recent developments in understanding the relationship between filler morphology, ink rheology, print parameters (i.e. nozzle size and print speed), and the resulting mechanical properties of printed epoxy composites. Novel deposition strategies to print hybrid composite/foam architectures and to control fiber orientation will also be discussed. Finally, the talk will conclude with a brief description of our current work applying the printing strategies developed for epoxy composites to preceramic polymer resins for the creation of high temperature ceramic composites. Current challenges and open questions will be highlighted throughout the talk.

# HYPERBARIC LASER CHEMICAL VAPOR DEPOSITION OF HIGH-STRENGTH ALUMINUM-SILICON-CARBIDE NANOCOMPOSITE FIBERS FOR AEROSPACE AND TRANSPORTATION APPLICATIONS.

James Maxwell, La Trobe University, E $\epsilon$ MC<sup>2</sup> Centre, Engineering Dept., Melbourne, Victoria, Australia  
j.maxwell@latrobe.edu.au

Avinash Baji, La Trobe University, E $\epsilon$ MC<sup>2</sup> Centre, Engineering Dept.

Ing Kong, La Trobe University, E $\epsilon$ MC<sup>2</sup> Centre, Engineering Dept.

**Key Words:** hyperbaric laser chemical vapor deposition, aluminum, silicon carbide, nanocomposite, fiber

For over 25 years, hyperbaric pressure laser chemical vapor deposition (HP-LCVD) has been studied by various authors as a mean for growing three-dimensional structures and fibers [1-2]. Novel normally-immiscible materials (NIMs) [3], amorphous/glassy ceramics [4], and high-strength fibers have been grown [5]. However, the highest experimental pressures to date have only reached beyond the critical point of certain alkanes (<60 bar) [6]. Our group has found it useful to synthesize materials from high pressure fluids, where the ensuing cooling rates after deposition can exceed 10<sup>6</sup> K/s. This has enabled the growth of (metastable) amorphous and nanostructured materials, including diamond-like carbon and boron carbides [7-8]. For this work, freestanding nanocomposite fibers were grown from mixtures of Bis(trimethylsilyl)methane and various organometallic and halide aluminum precursors. A chopped, cw fiber laser at 1064nm and diode lasers at 808nm were used for this work. The 1/e<sup>2</sup> laser beam waists were approximately 10-15 microns across. The resulting Al-Si-C fibers could be grown continuously—and were nanostructured due to the precursor pressures and laser powers employed. A variety of phases were found to be present, including aluminum carbide, silicon carbide, carbon, and silicon-rich phases. Scanning electron microscopy (SEM) and Energy Dispersive X-ray Spectroscopy (EDS) were used to characterize the composition and structure of the resulting materials. A map of the ternary phase diagram under these non-equilibrium conditions will be provided and discussed in detail. These fibers will find utility in reinforcements for ceramic- and metal-matrix composites for aerospace and transportation applications.

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## **COLD SINTERED CERAMIC COMPOSITES FOR MICROWAVE APPLICATIONS**

Ian M. Reaney, University of Sheffield, United Kingdom  
i.m.reaney@sheffield.ac.uk

Key Words: Cold sintering, ceramics, microwave

Cold sintering is a revolutionary processing technology that permits the densification of ceramics using a pressure mediated liquid phase at sintering temperatures  $<200\text{ }^{\circ}\text{C}$ . This contribution explores the potential of cold sintering for the fabrication of microwave (MW) materials and devices. We will demonstrate how cold sintering can be used to fabricate temperature stable ceramic composites suitable for dielectric substrates and RF components, resulting in properties either equivalent to, or superior than, conventionally sintered compositions. In addition, we will illustrate how cold sintering can be utilised to fabricate composites impossible by conventional processing. Finally, we demonstrate devices such as multilayer ceramic capacitors, graded index lenses and microstrip patch antennas fabricated using cold sintered ceramic composites.



# DESIGN OF CERAMIC-POLYMER OPTICAL COMPOSITES FOR BUILDING ENERGY EFFICIENCY INFRARED PROPERTY CONTROL AND TRANSPARENT BULK THERMAL INSULATORS

Paul G. Clem, Sandia National Laboratories, USA  
pgclem@sandia.gov

T.S. Luk, Sandia National Laboratories, USA  
E.D. Spörke, Sandia National Laboratories, USA  
S.Y. Chou, Sandia National Laboratories, USA  
T.E. Beechem, Sandia National Laboratories, USA  
P. Hopkins, University of Virginia, USA

**Key Words:** infrared, nanoparticle, thermal conductivity, emissivity, energy efficiency

Of ~\$1 trillion total U.S. energy use, 15% is for heating, ventilation and air conditioning, and over 20% of this energy, 3.4% of total US energy, goes out the window through thermal losses, equivalent to \$34 billion of energy waste annually. Materials design of windows, roofs and insulation is an opportunity for energy efficiency improvements, by optimizing solar absorption, transmission, infrared emission and thermal insulation. This presentation will discuss both static and dynamic/active approaches to improved energy efficiency in windows through materials design and performance improvements.

Topics will include:

- The solar spectrum and design of materials for windows to optimize UV/visible/infrared properties
- Approaches used for high performance static windows
- Emergence of dynamic (electrochromic, thermochromic) window technologies
- Approaches to minimize thermal conductivity in transparent materials
- Ceramic-polymer composites developed for energy efficient windows and future prospects.

Several groups in the U.S., including ours, have recently worked under the ARPA-E SHIELD program (Single-pane Highly Efficient Lucid Designs) on development of new materials for high efficiency window technologies including aerogels, optimized visibly transparent but infrared reflective coatings, and dynamic materials. In our presentation we will discuss new approaches to window materials as well as our development of two novel materials: thermochromic nanoparticle coatings and nanostructured, visibly transparent polymers.

Thermochromic materials enable environmentally-tuned windows – high infrared gain during cold temperatures and high infrared reflectivity/emission during warm temperatures. Nanostructured polymers have been developed as low cost, flexible, visibly transparent low thermal conductivity films as an alternative to aerogel technologies.

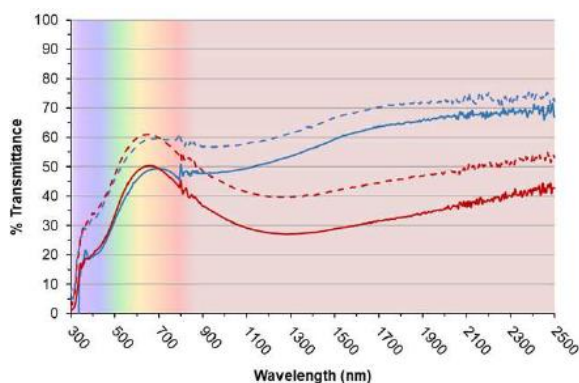


Figure 8 – Cold (top) vs. warm (bottom) transmission of thermochromic VO<sub>2</sub> films

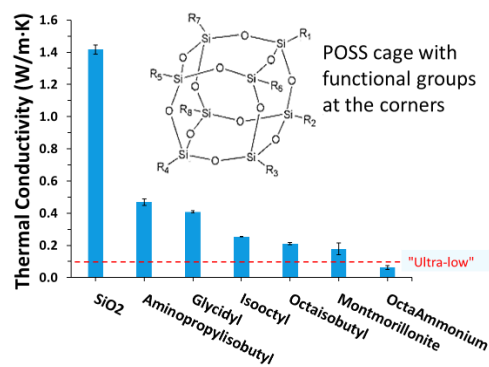


Figure 2 – Low thermal conductivity of POSS polyhedral oligomeric silsesquioxanes

This work was funded by the ARPA-E SHIELD program, Award No. DE-AR0000745  
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# **ENGINEERED MOLDING COMPOUND (EMC): OPTIMIZING THE DESIGN, PERFORMANCE, AND ECONOMICS OF CARBON FIBER COMPOSITES FOR INDUSTRIAL APPLICATIONS**

Jason Reese, Dow Chemical, USA  
jreese@dow.com

Dave Bank, Dow Chemical, USA

Patrick Blanchard, Ford Motor Company

Johnathan Goodsell, Purdue Composites Manufacturing and Simulation Center

**Key Words:** Molding Compound, Compression Molding, Automotive, Design, Validation

This work describes development of a new carbon fiber engineered molding compound (EMC) designed to be compatible with conventional high volume sheet molding compound (SMC) compression molding methods. The new material offers a threefold increase in elastic modulus compared to typical glass based SMC solutions. The increase in intrinsic stiffness enables section properties to be maintained within the constraints of a design package space. This allows for a low investment pathway to lightweight design using a process offering the design freedom of compression molding in combination with high volume of a premium reinforcement fiber. Each step of the process was optimized: chemistry reaction speed, resin impregnation into fiber, optimizing the sheet fiber orientation, translating sheet fiber orientation into molded part fiber orientation. To demonstrate the capabilities of the EMC solution, an automotive rear decklid assembly was built and tested to confirm performance and suitability for use in a high volume manufacturing scenario.

## BIOINSPIRED DESIGN OF STRUCTURAL AND THERMAL INTERFACE MATERIALS

Nima Rahbar, Massachusetts Institute of Technology, USA  
rahbar@mit.edu

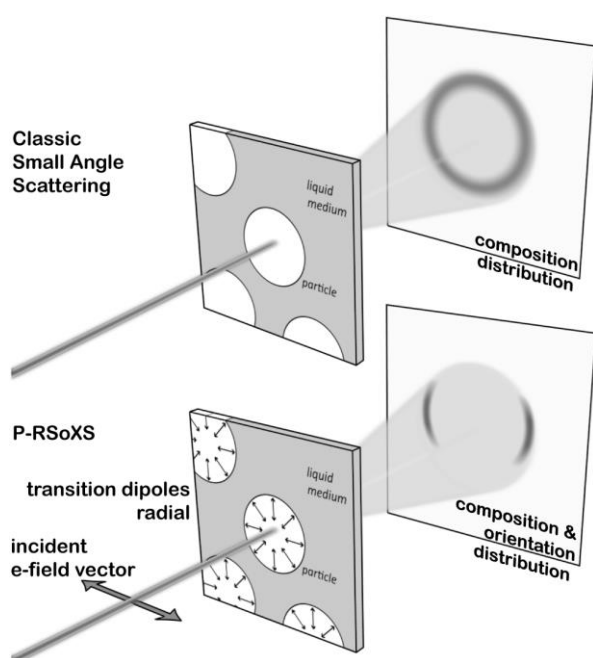
This talk focuses on the fundamental ideas arising from understanding the mechanisms behind the superior mechanical and thermal properties of biological materials through specific examples of nacre, bamboo, cartilage, and lipid bilayers. The mechanical behavior and toughening mechanisms of nacre-inspired multilayered materials are explored. In nacre's structure, the organic matrix, pillars and the roughness of the aragonite platelets play important roles in its overall mechanical performance. A micromechanical model for multilayered biological materials is proposed to simulate their mechanical deformation and toughening mechanisms. The modeling results are in excellent agreement with the available experimental data for abalone nacre. The highly nonlinear behavior of the proposed multilayered material is the result of distributed deformation in the nacre-like structure due to the existence of nano-asperities and nano-pillars with near theoretical strength. The application of this framework will be discussed for development of a new class of ductile cementitious fire resisting material, and a self-healing enzymatic concrete. Bamboo, a fast-growing grass, has higher strength-to-weight ratios than steel and concrete. The unique properties of bamboo come from the natural composite structure of fibers that comprises mainly cellulose nanofibrils in a matrix of intertwined hemicellulose and lignin called lignin-carbohydrate complex (LCC). Here we have experimentally and numerically studied mechanical and fracture properties of bamboo at multiple scale. We have utilized atomistic simulations to investigate the mechanical properties and mechanisms of the interactions of these materials in the structure of bamboo fibers. It is shown that a control hemicellulose model has better thermodynamic and mechanical properties than lignin while lignin exhibits greater tendency to adhere to cellulose nanofibril. Therefore, the role of hemicellulose found to be enhancing the mechanical properties while lignin provides the strength of bamboo fibers. Lastly, given the amphiphilic nature and chemical structure, phospholipids exhibit a strong thermotropic and lyotropic phase behavior in an aqueous environment. We performed non-equilibrium molecular dynamics simulations for a range of different temperature gradients. The results show that the thermal properties of the DPPC bilayer are highly dependent on the temperature gradient. Higher temperature gradients cause an increase in the thermal conductivity of the DPPC lipid bilayer. We also found that the thermal conductivity of DPPC is lowest at the transition temperature whereby one lipid leaflet is in the gel phase and the other is in the liquid crystalline phase. These results provide significant new insights into developing new thermal insulation for engineering applications.

## SOFT MATTER STRUCTURE MEASUREMENT BY POLARIZED RESONANT SOFT X-RAY SCATTERING

Dean M. DeLongchamp, National Institute of Standards and Technology, USA  
dean.delongchamp@nist.gov

Key Words: Nanocomposites, scattering, molecular orientation.

In many applications of soft matter, the connection between structure and performance is complex, and conventional structure measurements are not sufficient to provide a predictive structural model. Nanoscale variations in molecular orientation and composition, particularly in amorphous regions, are thought to be critical, but few techniques can probe them. I will describe our approach to polarized resonant soft X-ray scattering (P-RSoXS), which combines principles of soft X-ray spectroscopy, small-angle scattering, real-space imaging, and molecular simulation to produce a molecular scale structure measurement for soft materials and complex fluids. Progress and designs for a new P-RSoXS measurement station we are building at NIST beamlines at the National Synchrotron Light Source II will be shown.



*Figure 1 - Polarization at resonant conditions enables sensitivity to nanoscale orientation*

Results from model systems including commodity plastics and nanocomposites will be discussed. An emphasis will be placed on connections between P-RSoXS and small angle neutron scattering (SANS), including different contrast approaches, different experimental considerations, and unique measurement capabilities of each technique.

Our nanocomposite work involves polymer grafted nanoparticles as a critical model system. Polystyrene chains chemically grafted to gold nanoparticles make an important model system for printed dielectrics and a platform to study the fundamentals of grafted chain behavior. P-RSoXS measurements show a significant polarization dependence at energies near  $\approx 285$  eV, which is the energy of the polystyrene aromatic ring  $1s \rightarrow \pi^*$  resonance. Forward simulation shows that the ring planes must orient preferentially “face on” with respect to the particle surface. This behavior is consistent with the low graft density and the expected behavior of  $\pi$  electron-rich ring structures at noble metal surfaces. Some simulations showing bounds on the spatial extent of orientation will be shown. These results emphasize the new frontiers of characterization enabled by P-RSoXS in characterizing nanoscale chemistry and molecular orientation behaviors in composite materials.

# PROFILES IN LOCAL GLASS TRANSITION TEMPERATURE NEAR AND ACROSS POLYMER INTERFACES IN NANOSTRUCTURED BLENDS

Connie B. Roth, Emory University, Atlanta, USA  
cbroth@emory.edu

Key Words: polymer interfaces, glass transition, nanostructured blends, interfacial interactions, grafting.

Small domain sizes and adhesion between interfaces are the cornerstones of creating high performance multicomponent materials. Combined with an optimized morphology, the strategic use of interfacial interactions to perturb local properties is a promising avenue for creating designer materials where the desired global properties are obtained from an amalgam of local property changes. To achieve this grand goal, a detailed understanding of how interfaces perturb local properties are needed, along with knowledge of how the global macroscopic characteristics result from these local effects. This presentation will discuss our efforts to understand how various interfaces perturb local material properties and how different experimental techniques contribute to this picture.

Our group has employed a localized fluorescence method to measure the profile in local glass transition temperature  $T_g(z)$  across a glassy-rubbery polymer interface between polystyrene (PS) and poly(*n*-butyl methacrylate) (PnBMA) [1]. For a single interface between two semi-infinite domains, the local  $T_g(z)$  profile was found to be extremely broad and asymmetric, spanning 350-400 nm in extent as the local  $T_g(z)$  value transitioned the 80 K difference in bulk  $T_g$ s far from the interface from one side to another. Subsequent studies found this profile to be common to a range of weakly immiscible systems where the stiffer polymer domain with higher bulk  $T_g$  consistently showed a longer-ranged  $T_g(z)$  perturbation extending further from the interface [2]. The observed  $T_g(z)$  profiles were found to be strongly dependent on the interface formed between the two polymer domains during thermal annealing [2] and on the finite size of domains [3]. This difference between hard vs. soft interfaces, along with theoretical studies in the literature, has led us to investigate the  $T_g(z)$  profile in PS next to polydimethylsiloxane (PDMS) with varying crosslink density to systematically change the modulus of the neighboring domain without also changing the chemistry of the interface. We find the local  $T_g(z)$  in PS at a distance of  $z = 50$  nm away from the PS/PDMS interface can vary by 45 K when the PDMS modulus changes from  $\sim 1$  to 3 MPa.

These broad  $T_g(z)$  profiles demonstrating strong coupling of dynamics across the interface appear to only occur when the dissimilar polymer-polymer interface is well formed by annealing [2]. This suggests that some aspect during polymer interface formation (broadening of interface, chain interpenetration, or interfacial roughening) may be significant in controlling the observed behavior. Efforts to separate these different factors have led us to investigate silica substrates with rough interfaces and with end-tethered chains. We have observed similar long range  $T_g(z)$  profiles near PS end-grafted silica substrates, with the largest  $T_g(z)$  increase of 50 K next to the substrate corresponding to a low grafting density coinciding with the “mushroom-to-brush” crossover regime [4]. The  $T_g(z)$  profile is comparable to that observed near a polymer-polymer interface for a lower  $T_g$  polymer next to one with a much higher  $T_g$ , suggesting that chain connectivity across the interface is key to long range coupling of dynamics.

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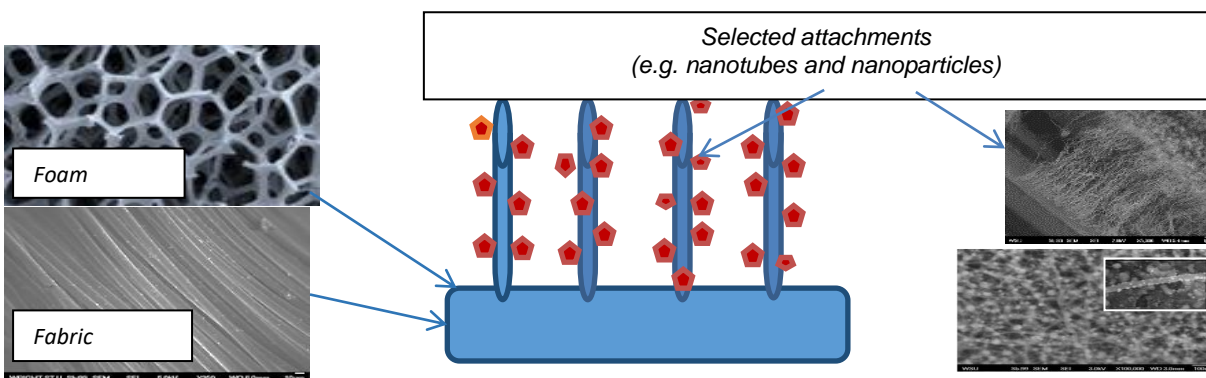
## HIERARCHICAL HYBRID MATERIALS FOR ROBUST & REUSABLE FUNCTIONAL DEVICES

Sharmila M. Mukhopadhyay, Mechanical & Materials Engineering, Wright State University, USA  
smukhopa@wright.edu

Keywords: surface modification, wettability and infiltration, nanotube carpets, multifunctional composites.

Nano-scale solids are known to offer significant advantages related to surface activity and quantum control, but their incorporation in engineering devices is often limited by challenges related to handling, storage and assembly combined with environmental proliferation risks. Many natural living systems address these challenges through elegant multi-scale hierarchical designs such as microvilli and dendrites, where a larger substrate is covalently anchored to progressively smaller functional entities. This type of architecture offers exceptionally high levels of solid-fluid interaction in very compact space for important functions such as load distribution, digestion, electrochemical exchange, and sensory behavior. However, this design has been traditionally avoided in engineered devices due to the complexities of creating primary bonds across components having different sizes, shapes and compositions to form a single continuous solid. In recent years, advances in surface science and nanoscale processing have made it possible for our team to fabricate these types of materials, which provide very significant advantages over conventional solids.

This talk will provide insights into selected materials that have shown promise in solid-fluid interaction devices such as catalysts, electrodes and sensors. A typical example is shown in Figure 1, where covalently bonded carpet-like arrays of electrically and thermally conducting carbon nanotubes (CNT) have been attached on porous carbon membranes using a two-step technique developed by this team. The nanotube carpets can create 1000-fold increase in surface area, without any significant change in weight or volume. These nanostructured surfaces can be further functionalized with selected coatings and catalytic nanoparticles for tailoring their fluid/matrix permeation, bio-interaction, chemical, catalytic, and electrical properties. Materials fabricated by this team have demonstrated unique properties suitable for a diverse variety of applications such as composite reinforcement, charge storage, gas and pathogen sensing, tissue engineering scaffolds, and water purification membranes.



*Figure 1: Example of durable and reusable hierarchical hybrid materials. Carbon nanotube carpets covalently attached on suitable surfaces such as graphitic foam (top left) or fabric (bottom left). Additional nanoparticles and coatings are attached based on functionality.*

## ORGANIC-INORGANIC HYBRID POLYMER COATINGS WITH CONTROLLED BIOFUNCTIONALITY

Svetlana A. Sukhishvili, Texas A&M University, Department of Materials Science & Engineering, USA  
svetlana@tamu.edu

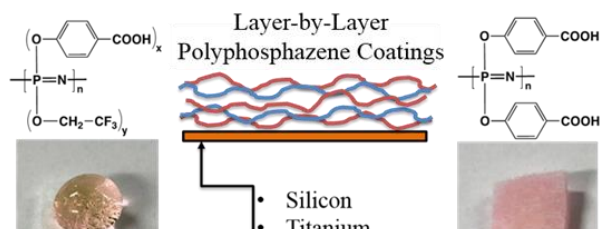
Victoria Albright, Texas A&M University, Department of Materials Science & Engineering, USA

Alexander Marin, Institute for Bioscience and Biotechnology Research, University of Maryland, USA

Alexander K. Andrianov, Institute for Bioscience and Biotechnology Research, University of Maryland, USA

**Key Words:** polyphosphazenes; self-defensive coatings; layer-by-layer; antibacterial films

Fluorinated polyphosphazenes (FPs) offer important advantages as biocompatible coatings for coronary stents and other biomedical devices. Recently, a new class of FPs has been introduced, which integrates carboxylic<sup>1,2</sup> or sulfonic acid<sup>3</sup> and fluorinated moieties into a single macromolecular structure. Assemblies of such fluorinated polyelectrolytes with polyelectrolytes or charged small functional molecules can offer efficient modulation of



**Figure 9 – Schematic representation of construction of LbL films of FPs and a polycation, as well as water contact angles of polyester surgical felt coated with 7-layer FP-terminated FP/poly(ethylene imine) films, in which FPs were 86% fluorinated (left) or nonfluorinated (right).<sup>1</sup>**

hydrophobicity, improved biocompatibility, as well as biofunctionality, such as modulated drug release.

Here, we have explored aqueous multilayer polyelectrolyte deposition as a convenient route to nanofabrication of layered coatings built from ionic FPs (iFPs) and polyelectrolytes<sup>1,2</sup> or small molecule partners. The resulting layer-by-layer (LbL) assemblies displayed controlled film growth, modulated hydrophobicity, swelling, and protein adsorption characteristics. Hydrophobic interactions largely contributed to the formation of LbL films of iFPs with polycations, leading to linear growth and extremely low water uptake. As shown in neutron reflectometry (NR) studies, films of fluorinated polyphosphazenes demonstrated superior layering and persistence of such layering in salt solution as compared to control

nonfluorinated polyphosphazene/polycation films. Hydrophobicity-enhanced ionic pairing between iFP and linear polycations gave rise to large-amplitude oscillations in surface wettability as a function of capping layer. Importantly, hydrophobicity of iFP-capped LbL coatings could be further enhanced by using a highly porous polyester surgical felt rather than planar substrates for film deposition.<sup>2</sup>

Moreover, because of the unique combination of ionic and hydrophobic properties, iFPs enabled direct LbL assembly with cationic antibiotics at neutral pH – a feature not achievable with traditional synthetic or biological hydrophilic polymers. The amount of antibiotics included in the coatings could be precisely tuned by coating composition and thickness. Importantly, antibiotics could be retained within the coatings for at least 30 days, and released in response to a trigger that indicated the onset of bacterial colonization, such as locally induced acidification. In addition, the coatings have demonstrated extremely low hemolytic activity (<1%), and were nontoxic to fibroblasts. Taken together, the data suggest that iFPs are versatile building blocks for creating surface coatings with controllable interfacial adhesion, wettability, and programmable interactions with biological milieus, including bacteria-triggered release of antimicrobials for prevention of bacterial colonization of surfaces.

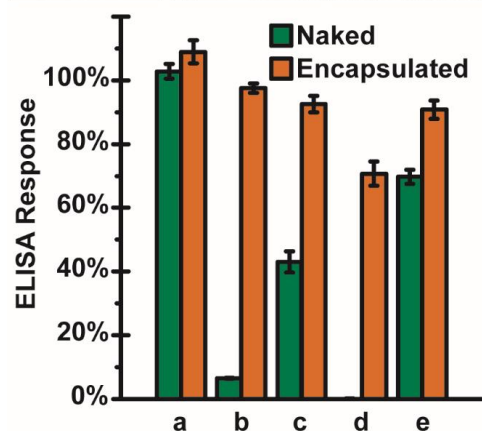
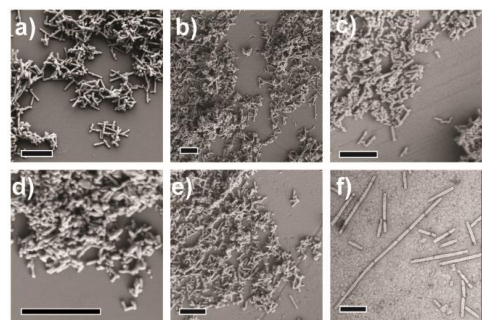
**Acknowledgement:** This work is supported by the National Science Foundation under Award DMR-1808483.  
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# PROTEIN-BASED DRUG DELIVERY AND THERMAL PROTECTION VIA MOF ENCAPSULATION

A/Prof Jeremiah J Gassensmith, The University of Texas at Dallas, USA  
gassensmith@utdallas.edu

Key Words: Biomimetic mineralization, Metal-organic Frameworks, Cold-chain remediation, Drug delivery



Top: SEM images of TMV@ZIF a) non-stressed, b) heating at 100 °C for 20 min, and after soaking overnight in c) methanol, d) 6 M guanidinium chloride, and e) ethyl acetate. Scale bars represent 2  $\mu$ m. f) TEM image of exfoliated non-stressed TMV. Scale bar is 200 nm. Bottom: The ELISA response of naked and encapsulated TMV subject to no stress (a), heating (b), methanol (c), 6 M guanidinium chloride (d), and ethyl acetate (e). The percentages range from buffer blank (0% TMV) to non-stressed naked TMV (100% TMV).

Recently, we and others have shown mechanistically how metal-organic frameworks (MOFs) are biomimetically formed on the surface of proteins and, once encapsulated, these *bionanoparticles* show dramatic enhanced thermal stability and resistance to denaturation in organic solvents. Earlier this year my colleagues and I presented a perspective (ACS Nano 2018, 1, 13–23) on a vision of how this nanotechnology could help “*break the cold chain*” with regards to vaccine delivery. Over the intervening months, we have come to realize we sold our vision short in this perspective—bionanomaterials formed via this method *is capable of more*. Specifically, as we report, ZIF-8 nano-structured proteins are near ideal candidates for controlled delivery of native proteins via subcutaneous implantation while protecting them *in vivo* against premature degradation. This would challenge the status quo for therapeutic protein delivery because vaccines *are the largest market for therapeutic proteins in the world* and they are one of the few medicines that are both shipped to places where 24-hour refrigeration is required yet not always available. Further, vaccines often require *multiple administrations* which means that a patient needs to return to a doctor. It has been suggested, however, that slow administration via time-release of vaccines may be a way to skip these multiple trips to the doctors. In developing nations, where infrastructure and trained medical professionals are scarce, this could be a lifesaving boon.

I will be discussing the comprehensively studied the thermal and chemical stability of MOF-based protein composites using a pre-clinical vaccine model based on tobacco mosaic virus (TMV). We demonstrate that biomimetic mineralization of ZIF-8 does not alter antibody binding to surface epitopes of the viral nanoparticle even after exposing the composite to 100 °C temperatures for 20 minutes. We then demonstrate that our MOF-vaccine composite, *can be directly injected into mice, produces a more linear dose response, and elicits an improved immune response as compared to pristine virus*. Imaging data show that ZIF-8 actually helps prolong release of the TMV over time, and we get a slightly improved immune response thanks to this unique drug delivery method. Histology shows the animal is left unharmed from even repeated administrations of the TMV@ZIF composite. Taken together, these data strongly suggest ZIF-8 based shells may provide a method to concurrently protect and deliver proteinaceous drugs safely.

## ADDITIVE MANUFACTURING OF MONOMER-FREE ORMOCER®-BASED COMPOSITES FOR DENTAL AND AUDIOLOGICAL APPLICATION

Dr. Herbert Wolter, “Dental and Micromedicine”, Fraunhofer Institute for Silicate Research (ISC), Germany  
herbert.wolter@isc.fraunhofer.de

Carina Kolb, “Dental and Micromedicine”, Fraunhofer Institute for Silicate Research (ISC), Germany  
Dr. Somchith Nique, “Dental and Micromedicine”, Fraunhofer Institute for Silicate Research (ISC), Germany

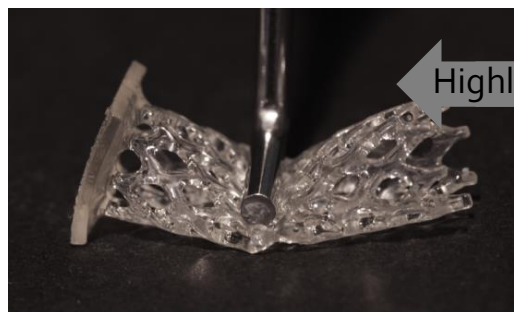
**Key Words:** Additive manufacturing, dental restoration, inorganic-organic hybridpolymers (ORMOCER®s), earmolds with thermoeffect

Additive manufacturing has a great potential, especially in the medical area where patient individual parts are required. However, there is still a lack of biocompatible materials which are printable and meet the high requirements of the targeted fields of end-use application (indirect dental restoration and earmolds). For this purpose, new types of inorganic-organic hybridpolymers (ORMOCER®s) with the indispensable biocompatibility, combined with an adapted profile of properties, have been developed.

For earmolds (audiological application, s. Fig. 1), the resulting materials show a thermoeffect, i.e. stiff/hard at room temperature (for an easy handling/cleaning) and soft/flexible at body temperature (for a comfortable wearing). The minimal storage modulus is in the range of 15 - 99 MPa, the maximal storage modulus at room temperature is up to 2550 MPa, each determined by dynamic mechanical analysis (DMA). As the softening temperature (15 - 49 °C) is also outside the normal body temperature, other applications are possible. To achieve the aesthetic and mechanical properties for a permanent indirect dental restoration (e.g. a crown, tooth) the ORMOCER®-based resin was modified by incorporation of various filler types and sizes. Highly refractive nanoparticles like ZrO<sub>2</sub> were used to match the refractive index of the matrix material and the macroscopic dental glass particles to achieve the desired high, tooth-like translucency. Mechanical tests show a high flexural strength (up to 140 MPa) and a Young's modulus of 5.5 GPa, determined by three-point bending test referring to DIN EN ISO 4049:2009 (dry storage).



Figure 1: Earmolds with thermoeffect



Highly flexible

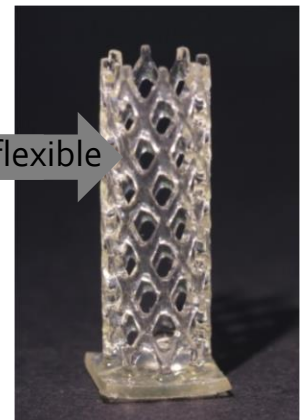


Figure 2: Stent-like structures with memory effect

For both types of material, 3D printing was successfully implemented by using Digital Light Processing (DLP) in combination with an optimized washing and final curing step. The filigree structure of the earmolds and the high-resolution of the occlusal structure of artificial teeth/crowns was possible.

Furthermore, 3D-printed stents (model, s. Fig. 2) based on materials with thermoeffect are a promising future application in the medical field. In particular, a memory effect arising from the thermoeffect of the material is crucial regarding the ability to unfold the compressed and stiff stent when it is implanted into the body by raising the temperature to 37 °C.



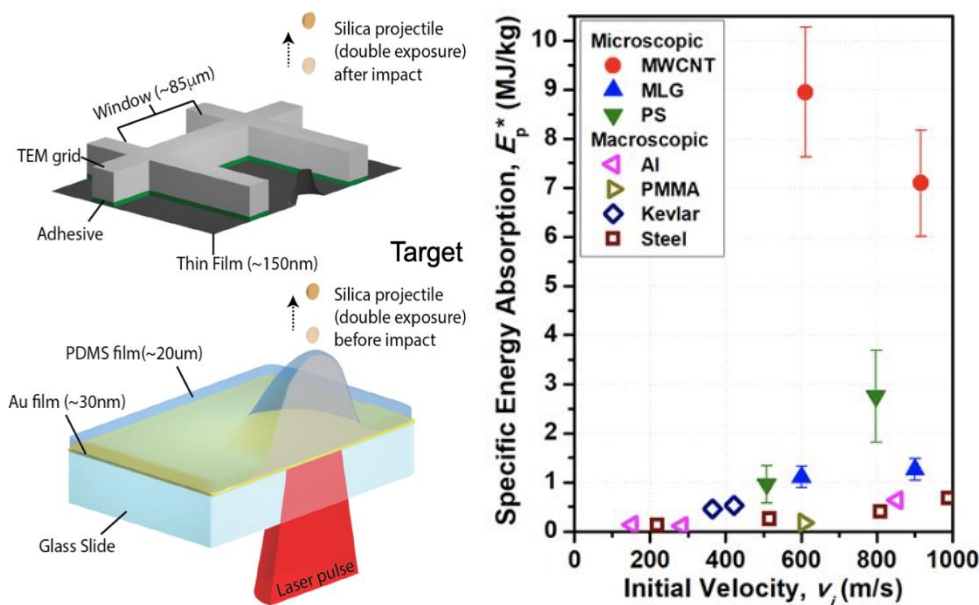
# HIGH RATE DEFORMATION BEHAVIOR AND EXTRAORDINARY ENERGY ABSORPTION OF CARBON NANOTUBE MATS AND GLASSY POLYMER THIN FILMS

Edwin Thomas, Rice University, USA  
elt@rice.edu

Jinho Hyon, Rice University, USA  
Olawale Lawal, USAF Academy  
Jason Streit, AFRL, WPAFB  
Richard Vaia, AFRL, WPAFB

**Key Words:** Ballistic impact, characterization, energy dissipation

We investigate the energy absorption characteristics and associated deformation behavior of free standing thin films using a micro-projectile impact test for two different materials: (1) multiwall carbon nanotubes (MWCNTs) and (2) glassy polystyrene. Films from 50-250nm thickness are impacted with silica microprojectiles at velocities from 300-900 m/s. The interconnected network of multiwall carbon nanotubes (MWCNT) sample while having quite modest quasi-static mechanical properties shows strong energy absorption at the extreme strain rates resulting from ballistic impact. As the spherical projectile engages the film, the bundles of MWCNT tubes straighten and translate into the impact region, dissipating the kinetic energy of the projectile via frictional interactions between tubes and stretching of the network, ultimately leading to fracture of principal tubes. The specific energy absorption depends on velocity and film thickness and can range up to 9 MJ/kg. For glassy, well entangled high molecular weight polystyrene, the impact of a supersonic micro-projectile initiates extensive crazing, yielding, and adiabatic heating leading to plastic flow of the load-bearing viscoelastic melt prior to film rupture and perforation. The less entangled, more mobile near-surface regions of these freestanding films favorably modify the deformation processes, increasing the specific energy absorption with decreased film thickness and increased impact velocity to impressive values of 2-3 MJ/kg for what is normally considered a brittle material.



(left) Laser Induced Projectile Impact Test (LIPIT). (right) Specific energy absorption of macro membranes and 50-1250 nanometer thick films.

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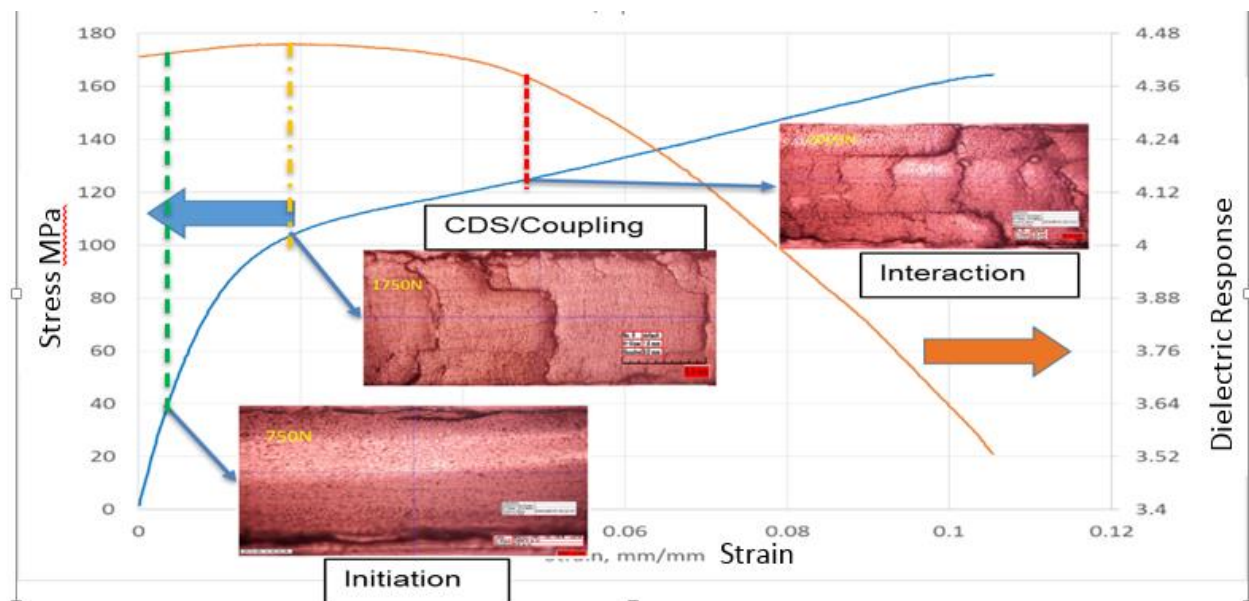
# DEFECT COUPLING: THE LAST FRONTIER IN PREDICTING THE STRENGTH, LIFE, AND DURABILITY OF FIBER REINFORCED COMPOSITE LAMINATES

Kenneth Reifsnider, University of Texas Arlington, USA  
kenneth.reifsnider@uta.edu

MD Russel Raihan, University of Texas Arlington, USA  
Vamsee Vadlamudi, University of Texas Arlington, USA

Key Words: Discrete defect coupling, durability

After more than 30 years of careful experimental investigation and exhaustive development of discrete damage analysis methods including integrated computational mechanics methods, our community knows a great deal about how discrete defects such as matrix cracks and defect growth (e.g. delamination) can be predicted. But many practical situations controlled by laminated multiaxial composite structures, the loss of performance and “sudden death” end of life is controlled by defect coupling which becomes a precursor to fracture plane development. Until recently, analysis methods to address such complex interaction and coupling of multiple defects and experimental methods of following the details of such interaction sequences as a foundation for understanding and model validation were not available. We believe that this barrier has been largely removed by recent work.



The figure illustrates the direction of our discussion. The stress-strain curve was recorded for tensile loading of a (+45,-45)s glass epoxy laminate loaded to failure. The insets show edge replica recordings of the damage development during this large deformation-to-failure test, including matrix cracking (and saturation) followed by crack coupling leading to fracture. The red curve presents measured values of through-thickness dielectric permittivity, which we have discovered reverses its direction of change with strain (from increasing to decreasing) exactly when defect coupling begins. Our discussion will present our efforts to interpret these results and to use our understanding to construct the first discrete defect simulation models followed by multiphysics modeling to predict this behavior (for the first time, to our knowledge). These and other examples are used to discuss our current level of understanding of this coupling as a precursor to the “beginning of the end” of performance of structural composite laminates.

## **TRICOMPONENT COMPOSITES WITH CELLULOSE NANOCRYSTALS AND CHITIN NANOFIBERS – EXPLORING POTENTIAL SYNERGY THROUGH COMPONENT INTERACTIONS**

Meisha L. Shofner, Georgia Institute of Technology, School of Materials Science and Engineering and  
Renewable Bioproducts Institute, USA  
meisha.shofner@mse.gatech.edu

Cameron W. Irvin, Georgia Institute of Technology, School of Materials Science and Engineering and  
Renewable Bioproducts Institute, USA

Chinmay C. Satam, Georgia Institute of Technology, School of Chemical and Biomolecular Engineering and  
Renewable Bioproducts Institute, USA

J. Carson Meredith, Georgia Institute of Technology, School of Chemical and Biomolecular Engineering and  
Renewable Bioproducts Institute, USA

**Key Words:** Cellulose nanocrystals, Chitin nanofibers, Bio-based materials, Interfacial interactions, Mechanical testing

Bio-based materials are being investigated increasingly as alternatives for synthetic materials in a variety of application areas, including composite materials. Among the options for bio-based materials, cellulose and chitin are abundant and increasingly available in different forms, including nanofibers. Due to their anticipated mechanical properties and anisotropic structure, nanofibers of cellulose and chitin lend themselves naturally for use as reinforcing fillers in polymer matrix composites, and the use of each in composites has been studied. However, composites containing both nanofillers has been explored to a lesser extent, and this composite design may provide benefits beyond those seen when the nanofibers are used separately. Therefore, the objective of this work is to examine how nanoscale forms of cellulose and chitin may be used separately and together in composite constructs. Specifically, we are preparing and characterizing composites composed of cellulose nanocrystals (CNCs) and/or chitin nanofibers (ChNFs) in a poly(vinyl alcohol) (PVA) matrix to understand more fully how component interactions affect the structure-property relationships in these materials and how these interactions may be used to produce synergistic improvements. For the specific CNCs and ChNFs used in this work, the nanofillers have opposite surface charge, with CNCs having a negative surface charge and ChNFs having a positive surface charge. Additionally, the components have an ability to interact through hydrogen bonding. These different types of interactions are anticipated to play a role in the structural development in the composites through the processing steps. To probe the effect of these interactions further, we have studied consolidated films as well as hydrogels. The results of these studies indicate that composites containing certain CNC/ChNF ratios possess better mechanical properties than composites containing only one type of nanofiber. Additionally, composites containing CNC/ChNF ratios where surface charges are more evenly balanced experience increased aggregation, presumably due to charge-driven association between the fillers. Mechanical property trends in consolidated films and hydrogels were qualitatively similar, suggesting a general behavior resulting from the component interactions.

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# PRECISE 3D STRUCTURING OF POLYMER NANOCOMPOSITES USING TRIAXIAL MAGNETIC FIELDS

Namiko Yamamoto, Department of Aerospace Engineering, the Pennsylvania State University, USA  
nuy12@psu.edu

Yagmur Atescan, Department of Aerospace Engineering, the Pennsylvania State University, USA

**Key Words:** Nanocomposites, magnetic assembly of nanofillers, multi-functionality

Polymer nanocomposites have been sought after for their light weight, high performance (strength-to-mass ratio, renewability, etc.), and multi-functionality (actuation, sensing, protection against lightning strikes, etc.). Nano-/micro-engineering has achieved such advanced properties by controlling crystallinity, phases, and interfaces/interphases; hierarchical structuring, often bio-inspired, has been also implemented. While driven by the advanced properties of nanofillers, properties of polymer nanocomposites are critically affected by their structuring and interfaces/interphases due to their small size ( $< \sim 50$  nm) and large surface area per volume. Measures of their property improvement by nanofiller addition are often smaller than theoretically predicted. Currently, application of these novel engineered materials is limited because these materials cannot often be made in large sizes without compromising nano-scale organization, and because their multi-scale structure-property relationships are not well understood.

In this work, we study precise and fast nanofiller structuring with non-contact and energy-efficient application of oscillating magnetic fields. Magnetic assembly is a promising, scalable method to deliver bulk amount of nanocomposites while maintaining organized nanofiller structure throughout the composite volume. In the past, we have demonstrated controlled alignment of nanofillers with tunable inter-assembly distances with application of oscillating one-dimensional magnetic fields ( $\sim 100$ s of G), by taking advantage of both magnetic attraction and repulsion. The low oscillation frequency ( $< 1$  Hz) was tuned to achieve maghemite nanofiller alignment patterns, in an epoxy matrix, with different amount of inter-nanofiller contacts with the same nanofiller volume fraction (see Figure 1a). This work was recently expanded to three-dimensional assembly using a triaxial Helmholtz coil system (see Figure 1b); the system can apply the triaxial magnetic fields of varying magnitude (max.  $\pm 300$ G,  $\pm 250$ G,  $\pm 180$ G (x-y-z)) and frequency (0 to 1 Hz,  $\sim 0.1$  Hz resolution) with controlled phase delay to the sample size of  $1.5'' \times 2.5'' \times 3.5''$ (x-y-z). Two model systems are currently studied: maghemite nanofillers in an elastomer for magnetoactuation, and nickel-coated CNTs in an thermoset for mechanical and transport property reinforcement. The assembled nanofiller structures are currently characterized by microCT; microCT scan data (see Figure 1b) are segmented through a machine learning algorithm, and will be modeled for their transport properties using a Monte Carlo method. These estimated properties will be compared with the experimentally characterized mechanical, transport, and actuation properties, providing the structure-interphase-property relationships. In future, we plan to integrate these nanocomposites to CFRPs for interlaminar property reinforcement, possibly with an out-of-autoclave composite processing.

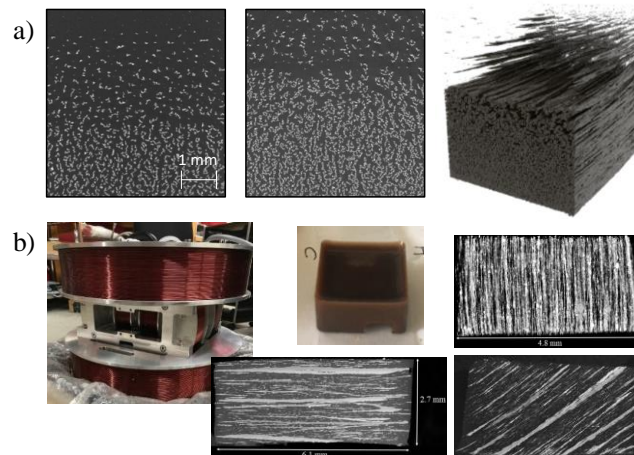


Figure 1. Magnetic tailoring of polymer nanocomposites and their microCT scans.

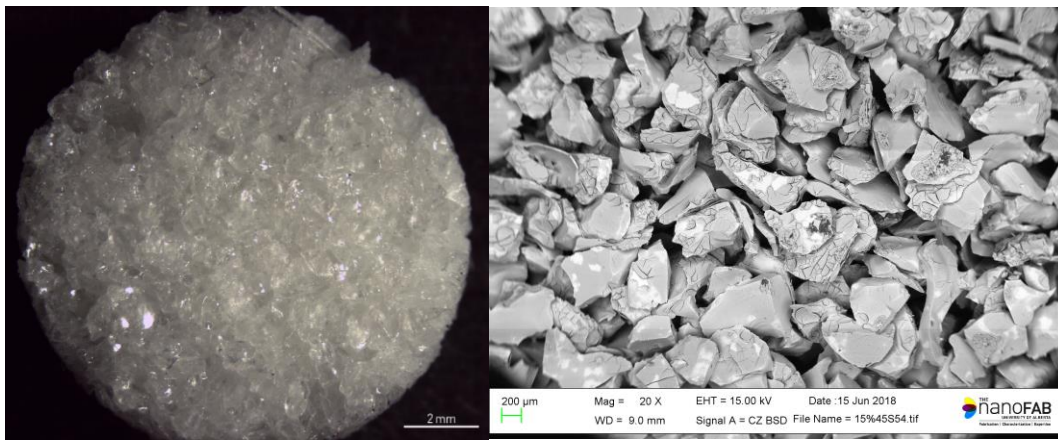
## CERAMIC COMPOSITE BONE TISSUE SCAFFOLDS

John A. Nychka, University of Alberta, Department of Chemical and Materials Engineering, Canada  
jnychka@ualberta.ca

Caitlin M. Guzzo, University of Alberta, Department of Chemical and Materials Engineering, Canada

Key Words: bioactive glasses, bone tissue scaffolds

The repair of broken or diseased bone tissue requires a multitude of strategies ranging from allografts to bone substitutes. Herein we describe a process to create porous all-ceramic scaffolds for bone tissue repair without the need for typical ceramics processing techniques for consolidation (see Figure 1)—a technique that has potential to be used *in situ* in the operating theatre or in the field. The process uses room temperature and pressure to elicit a reaction within a liquid ceramic precursor to form a silicate-glass binder phase to consolidate bioactive glass frit (of the 45S5 composition). Morphological characterization and mechanical response of the composite scaffolds is reviewed paying credence to design specifications required in biomedical implant materials, such as: formability, structural integrity, porosity, load-bearing capability, bioactivity, and resorbability.



*Figure 10. The liquid precursor solidifies in air to bind the 45S5 bioactive glass particles together into a rigid compact. (left) Macrograph of the porous composite scaffold; (right) back-scattered scanning electron micrograph of the porous composite scaffold.*

## IMPROVED MECHANICAL PERFORMANCE OF A NEXT-GENERATION HYBRID BONE ADHESIVE

Alina Kirillova, Department of Mechanical Engineering and Materials Science, Duke University, USA  
alina.kirillova@duke.edu

Ken Gall, Department of Mechanical Engineering and Materials Science, Duke University, USA

**Key Words:** bone adhesive, biomedical materials, bioresorbable bone adhesive, bone repair, hybrid materials

Bioresorbable bone adhesives have potential to revolutionize the clinical treatment of the human skeletal system, ranging from the fixation and osseointegration of permanent implants to the direct healing and fusion of bones without permanent fixation hardware. Despite a clear unmet need, there are currently no bone adhesives in clinical use that provide a strong enough bond to wet bone, while possessing good osteointegration and bioresorbability. We have recently introduced a novel, bioinspired mineral-organic bone adhesive (Tetranite®) based on tetracalcium phosphate and phosphoserine that cures in minutes in an aqueous environment and provides high bone-to-bone adhesive strength.[1] This new hybrid, bioresorbable material was measured to be 10 times more adhesive to bone than bioresorbable calcium phosphate cement and 7.5 times more adhesive than non-resorbable PMMA bone cement, both of which are standard of care in the clinic today.

In this study, we further explore the mechanical performance of the bioresorbable bone adhesive and aim to achieve its improved fatigue behavior that would facilitate its widespread clinical use *in vivo*, where dynamic loading is prevalent.[2] Aside from several studies discussing the fatigue behavior of calcium phosphate bone cements, this is the first study exploring and improving the fatigue behavior of bioresorbable bone adhesives.

For this purpose, we introduce polymeric materials into the bone adhesive – we reinforce it with PLGA polymer fibers and sutures as well as chitosan lactate aqueous solution. Apart from static mechanical testing and micro-CT analysis of different material formulations, we present a comprehensive study of the fatigue behavior of unreinforced and reinforced bone adhesive in compression at different conditions and point out the most promising formulations for further use in biomedical applications (Figure 1). The interplay between the different mineral-organic and polymer-ceramic components of the composite material leads to a significant improvement of the material's fatigue life under conditions mimicking the *in vivo* ones. Ultimately, the proposed functional composite formulations could aid in revolutionizing the procedures in which bone regeneration or fixation is critical for treatment and provide new design concepts for next generation biomedical materials with improved fatigue life.

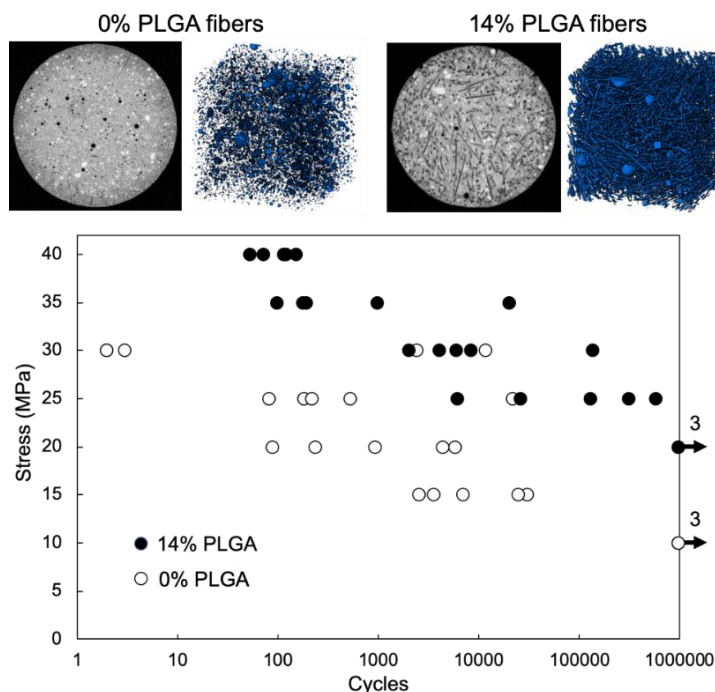


Figure 11 – Micro-CT images and compressive fatigue stress-life curves for the bone adhesive with 0% and 14% PLGA fibers

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## NATURAL FUNCTIONALLY-GRADED COMPOSITES IN HARD-TO-SOFT TISSUE (BONE-TENDON) JUNCTIONS

Linn W. Hobbs, John F. Elliott Professor Emeritus, MIT, Cambridge, MA, USA  
hobbs@mit.edu

Willie Mae Reese, University of California, Berkeley, CA, USA  
Alexandra E. Porter, Imperial College London, UK

Composite materials are often functionally engineered to imbue desired mechanical properties in materials for structural applications. Nature has long engaged in such composite engineering of biological organisms, which has evolved in both *flora* and *fauna* in response to specific mechanical demands. Incorporation of phenolic compounds (like lignin) in stiffening cell assemblies in plant basts, or of silica in plant leaves to resist chomping insect incursions, are good examples in the plant world. Skeletal bone in vertebrates is the classic example in the animal kingdom, a composite of flexible fibrous polymerized organic protein and platy-crystalline inorganic mineral that results in a mechanically strong, hard, tough tissue.

The musculo-skeletal system of vertebrates in fact comprises a variety of *both* hard and soft tissue types (bone, cartilage, tendon, ligament), generative cell types (osteoblasts, chondrocytes, tenocytes, fibroblasts, all of which can derive from multipotent mesenchymal stem cell precursors), and fibrous connective-tissue proteins (chiefly collagen, types I and II) that are susceptible to varying degrees of mineralization. In the case of bone, mineralization is extensive and forms a bi-continuous composite of mineral (chiefly partially-carbonated hydroxyapatite  $[\text{Ca}_{10}(\text{PO}_4\text{CO}_3)_6(\text{OH})_2]$  and precursors) and collagen (a triple  $\alpha$ -helix polypeptide) that self-assembles into protein fibrils (mostly type I collagen). Bone continually remodels itself and also re-forms as a consequence of injury or around implanted prostheses (such as knee and hip prostheses). High-resolution analytical TEM reveals [1] a mineralization mechanism which entails initial creation, at the mitochondria of bone-forming cells (osteoblasts), of pre-packaged vesicles that fill with a calcium-phosphate hydrogel and thereafter migrate through the cell wall. The vesicle contents subsequently crystallize [2] in the extra-cellular space with the dissolution of the vesicle containment wall, shortly before self-assembling collagen is expressed from the osteoblasts, providing a “just-in-time” ready source of Ca and P for mineralization of collagen fibrils with close to (though not identical with) the Ca/P ratio of hydroxyapatite found in the mature bone composite.

The critical *connective junctions* between different tissue types in the musculo-skeletal system (bone, cartilage, tendon, muscle, ligament) involve several hard-tissue/soft-tissue interfaces, characterized by *gradients* in mineralization, cell type, cell morphology, and collagen self-assembly modes. For example, standard procedure for re-attachment of ruptured tendons—by surgically re-locating the tendon proximally to bone—re-establishes the important bone-tendon junction (*enthesis*) in a period of about one year. The process proceeds through growth, contiguous to the (fully mineralized) bone surface, of a *partially*-mineralized fibrocartilage layer (comprising collagen, expressed by chondrocyte cells, that self-assembles into principally Type II and Type X collagens). TEM [3] of ovine models shows that mineralization of this cartilaginous layer appears to occur *via* the identical mechanism established [1,2] for bone mineralization but initiated instead by chondrocyte cells. SEM [3] reveals that the cell-type in the remaining *unmineralized* cartilage portion gradually morphs into tenocytes, which form more elastic tendon fibers comprising, again, mostly Type I collagen (but also Types III, IV, V and IX self-assembly motifs). The resulting hard-tissue/soft-tissue enthesis junction is thus seen [3] to be a *multiply graded* interface involving three different cell types, several different collagen self-assembly motifs, and the *functional gradation* of a composite material paradigm spanning fully-hard tissue (bone) to fully-soft tissue (tendon).

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## HOW BIG SHOULD YOUR NANOINDENTATION BE? THE IMPLICATIONS OF INDENTATION SIZE IN ASSESSING THE PROPERTIES OF COMPLEX STRUCTURES.

David F. Bahr, School of Materials Engineering Purdue University, USA  
dfbahr@purdue.edu

Raheleh Mohammad Rahimi, School of Materials Engineering Purdue University, USA

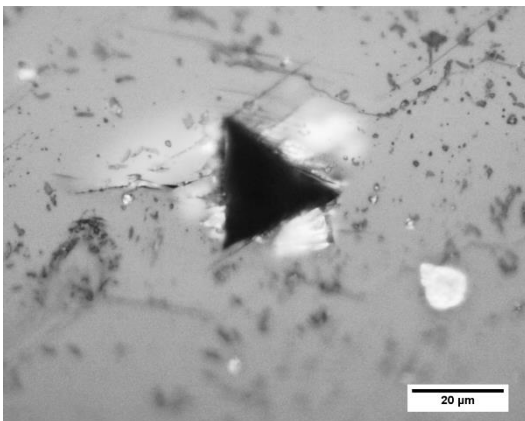
Alexandra C. Burch, School of Materials Engineering Purdue University, USA

Siavash Ghanbari, School of Materials Engineering Purdue University, USA

**Key Words:** Indentation, residual stresses, dual phase steels, energetics

Drivers for testing small volumes of materials for assessing the mechanical properties are either (1) the sample you want to test is very small in the first place, such as measuring the hardness of a wear resistant coating which is in thin film form or (2) you can well-characterize a small volume or the small volume has some spatially distinct feature, such as probing properties near a grain boundary, or in two phase systems. Small scale mechanical testing using instrumented indentation generally requires minimal sample preparation and has high spatial fidelity, but creates complex loading states as opposed to uniaxial or biaxial applied stress methods. However, the ease of use and wide range of samples which are amenable for indentation testing has made this a common tool both for experimental assessment studies and for experimental validation of providing comparisons to simulations and predictions of mechanical properties.

This presentation will focus on two systems of interest that exemplify the ways instrumented indentation can be used to extract information regarding material properties and structures. First, for a case where samples are small, an experimental study of the elastic and plastic deformation mechanisms and fracture in small molecular crystals will be presented. Energetic and pharmaceutical materials are often non-cubic molecular crystals with complex polymorphs that exhibit brittle mechanical behavior, making machining test samples difficult. Nanoindentation has been used to assess properties of large (mm's) crystalline forms, but to grow large crystals requires processing conditions which are non-typical for industrial growth conditions. Testing sub-mm crystals, and accounting for orientation effects, will be shown and validated versus large crystals. Of particular interest is determining the size of indentations required to extract information regarding elastic properties as well as the limit for onset of fracture. By using two materials with very similar elastic properties but different fracture behavior (ioxuridine, a pharmaceutical; and HMX, and explosive), the importance of size in testing tablets and plastic bonded molecular crystals is emphasized.



The second system of interest is metallic materials, with sparse defects, two phase structures, and residual stress gradients. The effects of dislocation density on both yield behavior and subsequent plastic deformation, and the ability to probe spatially varying properties will be evaluated. Of particular interest will be the use of indentation systems to extract residual stresses in graded structures. The localized properties of particular grains and particular locations will be compared to broad x-ray measurements of stress, and while averages compare to the full field measurements, the local variations can be significant, with stress variations of over 25%.

*Figure 12 – Idoxuridine indented at 200mN showing slip, pile-up, and fracture*



## DIRECTIONS OF ZERO THERMAL EXPANSION IN ANISOTROPIC OXIDES

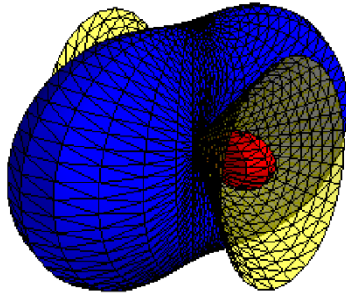
Scott J. McCormack, University of Illinois at Urbana Champaign, USA (currently at University of California)  
sjmccormack@ucdavis.edu

William A. Wheeler, University of Illinois at Urbana Champaign, USA

Benjamin S. Hulbert, University of Illinois at Urbana Champaign, USA

Waltraud M. Kriven, University of Illinois at Urbana Champaign, USA

Key Words: In-situ; X-ray diffraction; High temperature; Thermal expansion; Anisotropic properties



*Figure 13.* – Quadric surface visualizing the coefficients of thermal expansion of  $\text{HfTiO}_4$  at room temperature. Blue is positive, red is negative and yellow represents directions of zero thermal expansion.

Oxide materials often have anisotropic crystal structures, which can result in direction-dependent material properties. While they typically have positive coefficients of thermal expansion, it has been observed that some oxide materials can have directions of negative thermal expansion over certain temperature ranges. Such materials, having both positive and negative coefficients of thermal expansion, must also have particular directions in which the thermal expansion is zero. Using the Quadrupole Lamp Furnace (QLF) developed in the Kriven group at the University of Illinois at Urbana Champaign, high-temperature in-situ x-ray diffraction has been performed at the National Synchrotron Light Source II (NSLS II) X-ray powder diffraction beamline (XPD – 28-ID) to track directions of zero thermal expansion in orthorhombic  $\text{HfTiO}_4$ . These results have important implications for the design of composites for high-temperature applications.

# ACTIVATING EXTRINSIC AND INTRINSIC TOUGHENING MECHANISMS IN POLYCRYSTALLINE CERAMICS AND THEIR COMPOSITES VIA MICROSTRUCTURAL ENGINEERING

Jessica A. Krogstad, Department of Materials Science and Engineering at the University of Illinois Urbana-Champaign  
jakrogst@illinois.edu

Charles S. Smith, Department of Materials Science and Engineering at the University of Illinois Urbana-Champaign

Key Words: Twinning, Ferroelastic, In Situ Deformation, Microstructure, Toughness

Ferroelastic toughening is one of a limited number of intrinsic toughening mechanisms available for ceramics, yet rarely is it effectively implemented due to a limited understanding of the activation mechanisms within a polycrystalline framework. In the earliest descriptions of ferroelastic toughening, terms such as the transformation strain, coercive stress and process zone parameters were included following other (extrinsic) crack tip shielding models. In the years that have followed, constitutive models have become more sophisticated, incorporating crystal orientation, rate behaviors, and several other factors. However, further development of these models has been limited by the paucity of experimental observations linking ferroelastic switching with critical, yet common, microstructural variations (i.e. grain size, nearest neighbor orientations, secondary/grain boundary phases, etc.). Here we present a multi-scale experimental approach to explore the role of stress concentration, stress transfer and localized constraint in ferroelastic domain nucleation, motion and subsequent toughening. In situ TEM nanopillar and ex situ micropillar compression on single crystal specimens extracted from a polycrystalline ceramic have been used to correlate crystallographic orientation with coercive stresses for domain nucleation and motion. The comparison between these two length scales also highlights the importance of boundary conditions on the nucleation of ferroelastic domains and sheds light on the grain size dependence of domain nucleation probability extracted from Vicker's indentation of polycrystalline ceramics of the same composition. This insight will ultimately be coupled with grain orientation, elastic anisotropy data and quantified stress distributions during deformation to establish the early foundations of a microstructural design framework for ferroelastically toughened ceramics.

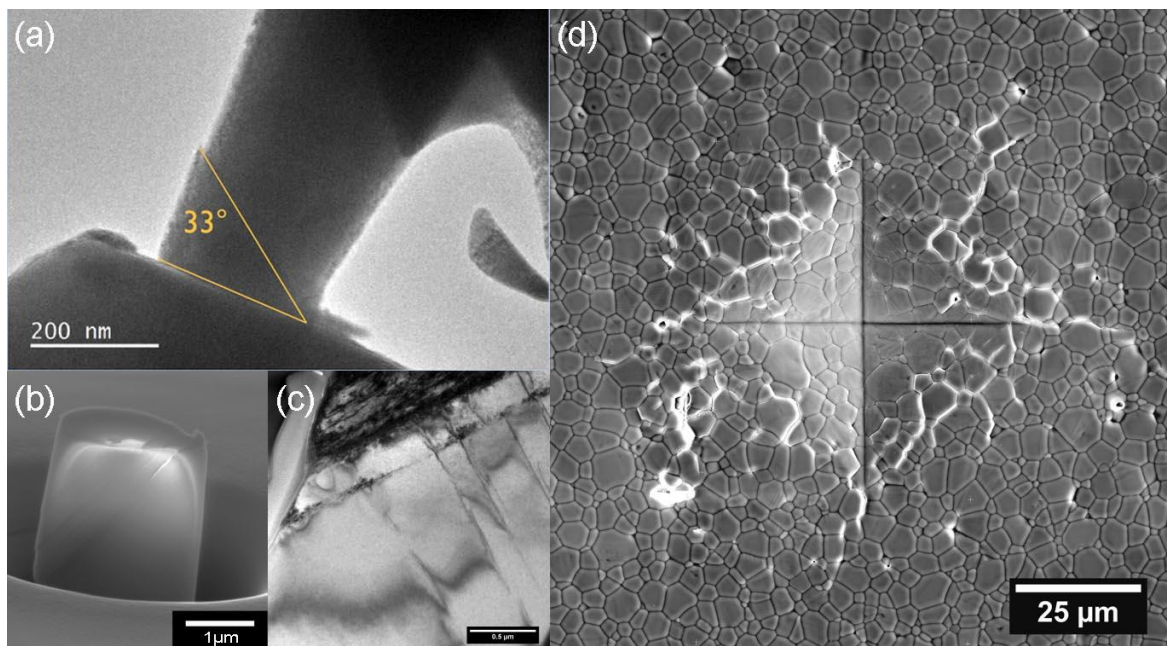


Figure 14 – An overview of the length scales probed in this study. (a) In situ single crystal nanopillar deformation as a function of crystal orientation. (b) Ex situ single crystal micropillar deformation at a lower surface to volume ratio. (c) TEM bright field imaging of the dislocation/twin structure following micropillar deformation. (d) Vickers indentation of a polycrystalline ceramic wherein twinning is observed in many but not all of the grains surrounding the indent.

# A NEW PARADIGM TO EVALUATE THE CLEAVAGE ENERGY OF BRITTLE MATERIALS

Dov Sherman, School of Mechanical Engineering, Tel-Aviv University, Israel  
dovsherman@tauex.tau.ac.il

Merna Shaheen-Mualim, School of Mechanical Engineering, Tel-Aviv University, Israel

Key Words: Cleavage energy; Brittle materials; Energy gradient; Dynamic bond breaking mechanisms; Kinks.

Crack initiation in brittle materials is usually dictated by the energy required to create two new surfaces. This energy is known as Griffith barrier and equals twice the free and relaxed surface energy,  $2\gamma_s$ . This value is usually taken as the cleavage energy for crack propagation as well. We investigated, experimentally, the fundamentals of cracks dynamics in brittle crystals, with emphasis on the cleavage energy at initiation and during propagation. Silicon crystal served as a model material, where two of its low energy cleavage systems (LECSs) were examined. During experiments, the gradient of the quasi-static energy release rate (ERR) for unit length of crack advance,  $dG_0/da \equiv Q$  (in units of  $\text{J/m}^2/\text{mm}$ ), was revealed as a new critical variable not discussed before, with a critical influence on the material property [1,3].

When loaded by low  $Q$  ( $< 0.5 \text{ J/m}^2/\text{mm}$ ), in air, a complex and diverse stress corrosion cracking (SCC) behavior was revealed; the cleavage energy strongly depends on  $Q$ , the environment and crystallographic structure. We further show that at  $Q > 0.7 \text{ J/m}^2/\text{mm}$ , the SCC mechanisms vanish for both LECSs, and the cracks initiate and propagate at cleavage energy higher than that in vacuum, or the Griffith barrier of  $2\gamma_s$ , twice the free surface energy of the cleavage plane. The highest values obtained in the experiments for the  $(110)[1\bar{1}0]$  and  $(111)[11\bar{2}]$  LECSs, were 1.47 and 2.14 times  $2\gamma_s \text{ J/m}^2$ , respectively (see Fig. 1). Surprisingly, the cleavage energy for initiation and propagation remain constant during the event of fracture for a prescribed  $Q$ , meaning, it is not crack speed dependent. Moreover, we show that all the variables participating dynamic cleavage are linearly dependent on  $Q$ , which provides the evidences that the ERR gradient is the controlling variable governs cracks dynamics. Report of cleavage energy should be accompanied by the value of  $Q$ . The variety of  $Q$  may explain the large scatter of the cleavage energy of silicon existing in the literature.

We suggest that the causality of the above fundamental behavior is laying on the way crack initiate and propagate at the atomistic scale, i.e., the bond breaking mechanisms in form of planar kinks with complex energy consumption mechanisms.

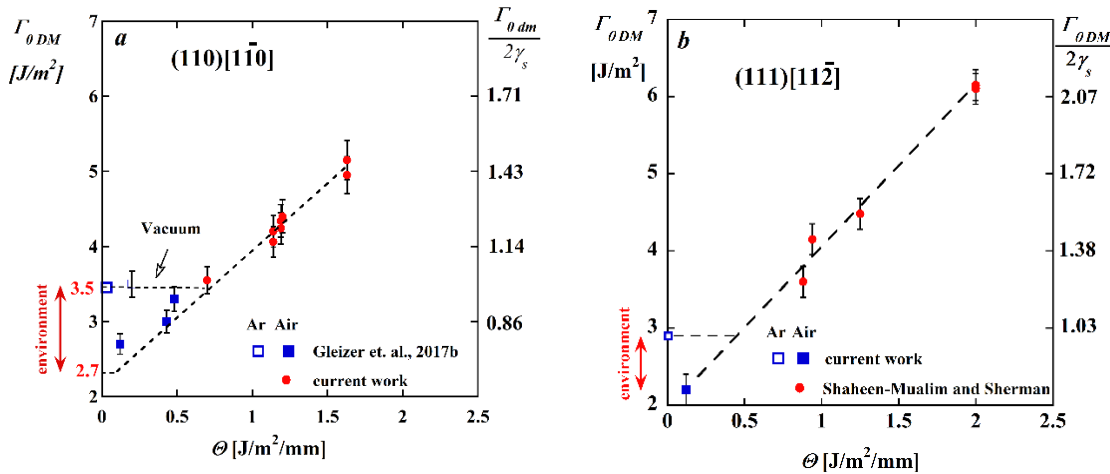


Fig. 1. The cleavage energy at initiation,  $G_{0DM}$ , as a function of  $Q$  and environment for the two LECSs of silicon crystal, a  $(110)[1\bar{1}0]$  and b, the  $(111)[11\bar{2}]$ .

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## STRATEGIES TO STRENGTHEN CERAMICS FOR WINDOWS AND DOMES

Ivar Reimanis, Colorado School of Mines, USA  
reimanis@mines.edu

Key Words: transparent, strength, toughness, spinel

Strengthening of transparent ceramics is highly constrained by the fact that the classic methods to toughen ceramics, via microstructure modification, increase light scattering. Nonetheless, improvements are possible when a composite approach is applied at the nanoscale. For example, attempts to toughen spinel by reinforcing with alumina show modest gains. This paper discusses those efforts and examines the possibility of applying the concept to other ceramics. Strategies and limitations for windows and domes, for which the transparency requirements are not as stringent as for some other optical applications, are discussed.

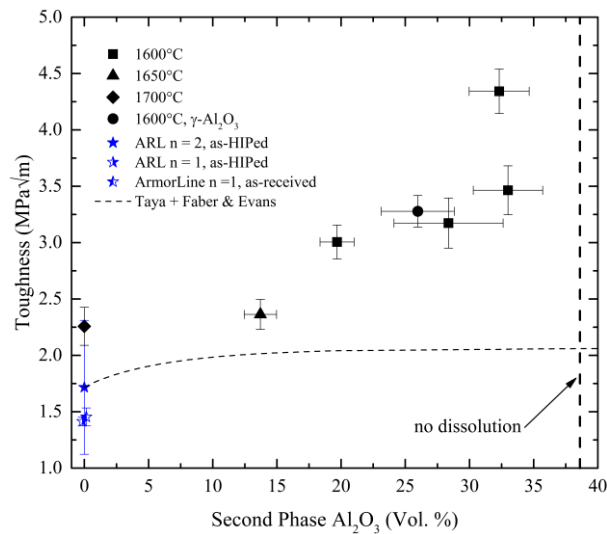


Figure 15 – Toughness for different spinels and spinel—alumina composites.

# **COSMIC COMPOSITES: ROCKS FROM SPACE AND THEIR ASTONISHING INFLUENCE ON EARTH AND HUMANITY**

Gregory A. Brennecka, University of Münster – Münster, Germany; Lawrence Livermore National Laboratory – Livermore, USA  
brennecka@gmail.com

Key Words: meteorites; incredible; influence; Earth; humanity

Meteorites are some of the most complex natural materials known. They are incredibly compositionally diverse rocks, ranging from chunks of almost pure iron and nickel metal, which derive from the cores of disrupted planetary bodies, to pristine collections of dust and ice that have existed virtually unmolested since the birth of the Sun. Certain types of meteorites contain the oldest materials ever dated, and some even host the direct remnants of previous generations of stars that contributed material to build our Solar System. Meteorites are time capsules of information about Solar System history and evolution, and, simply put, are a scientific treasure trove. In addition, whereas most meteorites come from the scores of planetary bodies that now reside in the asteroid belt, some even represent samples that originate directly from our Moon and Mars. However, although the value of information we have gained about Earth and the Solar System from studying meteorites as scientific objects cannot be underestimated, the principal importance of meteorites to humanity is far more complex due to their oftentimes spectacular arrivals and important payloads.

From a cultural perspective, many of the world's ancient empires and most popular religions have inflection points in which meteorites played an important role, in some cases drastically altering the course of history. Christianity was an obscure cult followed by relatively few people until a timely meteoritic interaction changed its trajectory. The most venerated object in the Islamic faith almost certainly has a meteoritic origin, and for a short time, worship of a meteorite (adorned with fancy dressings and gemstones) was even the official religion of the Roman Empire. Wars have been waged (and ended) due to encounters with extraterrestrial materials. Temples have been built to honor fallen stones, and early cultures were enamored by the metal found in meteorites, as they did not yet know how to produce such metal themselves. These numerous overlaps between humans and meteorites were critical in shaping modern culture around the world, yet the most important contributions of meteorites to Earth started happening shortly after the planet formed ~4.5 billion years ago.

If meteorites had not interacted with the Earth shortly after its formation, the Moon would not exist. Earth likely would not have liquid water at its surface or offer a habitable atmosphere. The continued bombardment of Earth by space rocks gives humans access to many of the precious metals crucial for modern technology—such as iridium, platinum, and gold—which would otherwise be thoroughly sequestered in Earth's core and inaccessible for exploitation. In addition, and probably most importantly, meteorites were the primary delivery vehicles for the complex organic materials that eventually created the biosphere. Many of the organic building blocks thought essential for the emergence of life are present in primitive meteorites, with one sample alone hosting over 80 amino acids (known life uses only 20 of these). In addition, multiple nucleotide bases of both RNA and DNA as well as other vital biomolecules have been discovered in extraterrestrial specimens, indicating that the building blocks of life could have been created abiotically in the outer Solar System and delivered to Earth via meteorites. And, of course, a meteorite impact was influential to ending the long reign of the dinosaurs, paving the way for mammals to rapidly evolve and thrive, promptly taking over the helm as Earth's dominant class of creature.

In this presentation, I will discuss the immense influence meteorites have had on our planet, spanning from its creation to modern human culture. In addition, I will highlight some of the incredible scientific insights we have gained from the study of these unique materials, and some of the active areas of research in reconstructing the history and evolution of our Solar System.

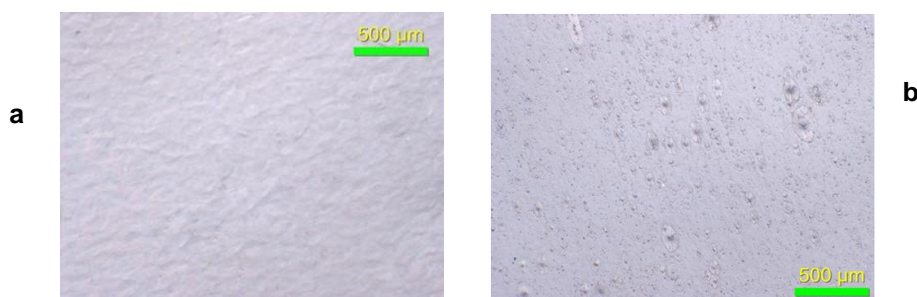
## PROCESSING AND STRUCTURE OF BOPP FILM WITH NANOPARTICLE-BASED ADDITIVES

Krishnamurthy Jayaraman, Dept. of Chemical Engineering & Materials Science, Michigan State University, USA  
jayarama@egr.msu.edu

Xing Lu, Dept. of Chemical Engineering & Materials Science, Michigan State University, USA  
luxing1@msu.edu

**Key Words:** nanocomposite, morphology development, crystallite size, barrier film, biaxial stretching

This paper reports on biaxially oriented polypropylene nanocomposite film produced by two different processes: simultaneous equi-biaxial stretching and sequential asymmetric biaxial stretching of extruded sheets of polypropylene layered silicate nanocomposites with 2 wt%, 5 wt% and 10 wt% of nanolayers. The nanolayers were coupled to the matrix polymer through solvent-free silane treatment of the organically modified montmorillonite and by the addition of maleated polypropylene; a masterbatch was prepared first and let down with the polypropylene homopolymer (MFR=8; melting temperature=167°C) in the sheet extrusion line. The first process of simultaneous equi-biaxial stretching was carried out on square pieces of 1.2 mm thick extruded sheet at 156°C in a Karo IV apparatus. Area stretch ratios of 45-50 were obtained in both stretching processes without breaking the film. This was achieved with a linear stretch ratio of 6.5 along each direction for the simultaneous equi-biaxial process and the resulting film was clear for the nanocomposite. The sequential stretching was carried out in a continuous line where the stretch ratio along the machine direction was 5, followed by a stretch ratio of nearly 10 along the transverse direction. While the equi-biaxial stretching process produced clear film without defects, the asymmetric sequential stretching process resulted in cavitated regions on the film—see Figure 1. The latter effect appeared during the transverse stretching step around submicron-sized nanolayer stacks. The mean aspect ratio and orientation of the nanolayers in the BOPP nanocomposite films were evaluated from TEM micrographs. The average crystallite size was obtained from X-Ray diffraction scans on the various BOPP films. The permeability to water vapor at 23°C and 100% RH as well as 75% RH was obtained in g-mil/m<sup>2</sup>-day from the MOCON 3/34 apparatus, using masks with an area of 5 cm<sup>2</sup>. A 50% to 75% reduction was obtained in the permeability to water vapor, depending on the loading of nanoclay, the process used and the multilayer configuration. The crystallite size was consistently larger in the BOPP film containing the nanoclay and the crystallite size was greatest in the film with the lowest relative permeability to water vapor.



*Figure 1. Optical micrographs of BOPP nanocomposite film with 5 wt% loading: (a) clear film from equi-biaxial simultaneous stretching -- 6.5 x 6.5; (b) film with spots from asymmetric sequential stretching -- 5 x 10*



## IMPARTING MACHINE INTELLIGENCE INTO DIRECT INK WRITE MANUFACTURING

Dr. J. Daniel Berrigan, U.S. Air Force Research Laboratory, USA  
Mr. Marshall V. Johnson, Georgia Institute of Technology, USA  
Dr. James O. Hardin, U.S. Air Force Research Laboratory, USA  
Dr. H. Clive Liu, UES, Inc.  
Dr. Surya Kalidindi, Georgia Institute of Technology, USA

Key Words: Direct Write, Additive Manufacturing, machine learning, image classification

While digital manufacturing methods such as computer numerical control machining and additive manufacturing have enabled the creation of small lots of components with various complex shapes and materials. Understated, is the degree of individual process engineering and expertise required to tune material behavior, processing conditions to achieve expected properties. Current robotic manufacturing control frameworks lack the sensing and autonomy to effectively perceive and decide a course of action in response to these dynamic manufacturing environments. As a result, many commercial platforms limit user control over materials to ensure repeatability at the cost of agility. This paradigm fundamentally prevents the maturation of processes like direct ink write (DIW) additive manufacturing, which has been used to 3D print tissue scaffolds, ceramics, metals, magnets, and free-form structures.<sup>[1-5]</sup> In DIW additive manufacturing, both the materials behavior and desired structure are constantly changing, but the machine itself is rigid and never “learns” from past experiences. In general, only the user learns, thereby creating experienced “super users”. Using DIW as an example, we will present how materials and printed device development spurred the push to address the gap between robot and human experience by combining image classification, adaptive feedback, and analytical methods. A generalizable image classification method was developed to characterize the spanning behavior of a thixotropic fluid printed across 2- and 3-D gaps. The automated classification informed how to adapt the tool path and subsequently predict printing conditions for log-pile structures. By harvesting the relevant data and outcomes with user context, we seek to build an open knowledge community to enable more task-agnostic direct ink write manufacturing.

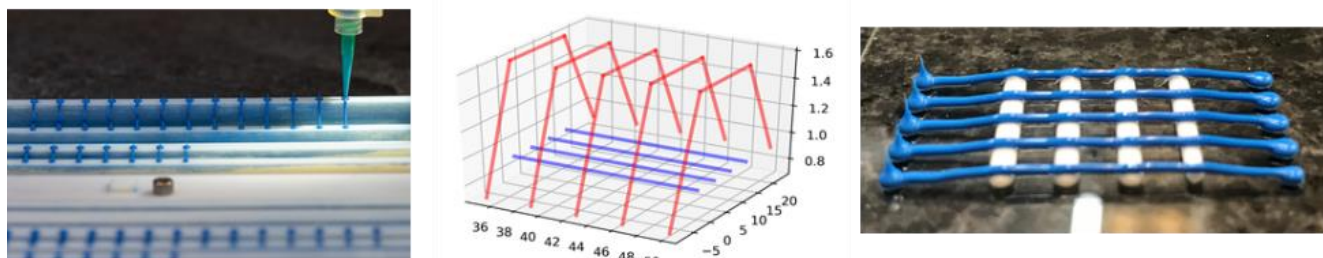


Figure 16 – The printer trains itself how to print a spanning feature on a pre-defined “obstacle course” (left), this information is use to predict tool path for a two-layer log pile structure of dimensions not included in the training set (middle). The structure is successfully printed and the image classifier verifies success (right).

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## BIOINSPIRED NANOCOMPOSITES: ORDERED 2D MATERIALS WITHIN A 3D LATTICE

Iryna Polishchuk, Department of Materials Science and Engineering, Technion Israel Institute of Technology, Israel

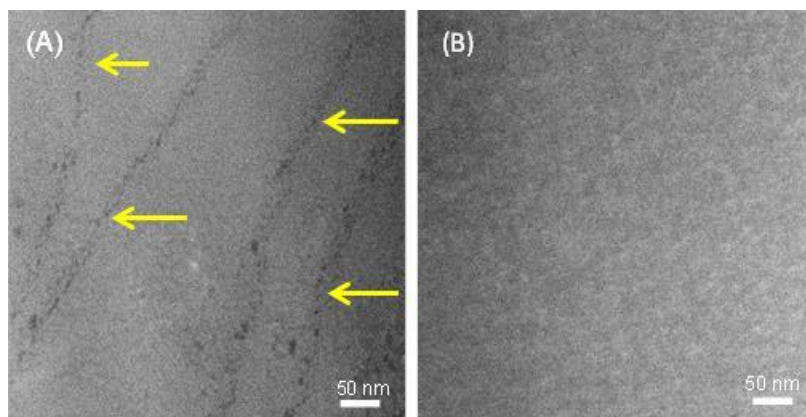
piryna@technion.ac.il

Giuseppe Falini, Department of Chemistry Giacomo Ciamician, University of Bologna

Boaz Pokroy, Department of Materials Science and Engineering, Technion Israel Institute of Technology, Israel

**Key Words:** bioinspired, nanocomposite, graphene oxide.

Advanced composites are used in a variety of industrial applications and therefore attract much scientific interest. We recently developed a novel carbon-based nanocomposite via incorporation of graphene oxide (GO) into the crystal lattice of single crystals of calcite [1]. Incorporation of a 2D organic material into single-crystal lattices has never before been reported. To characterize the resulting nanocomposites, high-resolution synchrotron powder X-ray diffraction, electron microscopy, transmission electron microscopy, fluorescence microscopy and nanoindentation tests are employed. A detailed analysis reveals a layered distribution of GO sheets incorporated within the calcite host (Fig. 1). Moreover, the optical and mechanical properties of the calcite host are altered when a carbon-based nanomaterial is introduced into its lattice. Compared to pure calcite, GO/calcite composite crystals exhibit lower elastic modulus and higher hardness. The results of this study show that the incorporation of a 2D material within a 3D crystal lattice is not only feasible but also can lead to the formation of hybrid crystals exhibiting new properties.



*Figure 1. HAADF-STEM image of calcite with embedded GO sheets appearing as dark stripes (A), and of pure calcite showing no Z-contrast (B). Arrows indicate GO sheets entrapped within the crystal.*

[1] Matteo Di Giosia, Iryna Polishchuk, Eva Weber, Simona Fermani, Luca Pasquini, Nicola M. Pugno, Francesco Zerbetto, Marco Montalti, Matteo Calvaresi, Giuseppe Falini and Boaz Pokroy. Bioinspired Nanocomposites: Ordered 2D Materials Within a 3D Lattice. *Adv Funct Mater* 2016; 26:5569.

## SCALING UP GRAPHENE PET NANO-COMPOSITES FOR INDUSTRY APPLICATIONS

Jay C. Hanan, Oklahoma State University, USA  
Jay.Hanan@okstate.edu  
Sudheer Bandla, Niagara Bottling LLC, USA

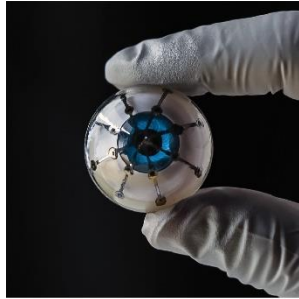
Graphene nanocomposites have offered promise to benefit manufactured goods and their packaging materials for over a decade. The promise includes improving thermal properties for processing, increased specific strength, enhanced barrier properties, and electrical conductivity. Often such improvements have a potential for implementation with very little change in industry standard processing equipment. As commodity and energy costs rise, efficient product design becomes increasingly important. Shipping and material costs have risen to a larger, and often leading, fraction of manufacturer's total costs. Simply using less material means less weight, which both reduces raw material and transportation costs. However, this is only possible if the new design performance meets or exceeds market needs. An additional benefit of material reduction is a reduced impact on the environment. Some specific examples of environmental impact reduction from the use of graphene based nanocomposites were recently measured at 30%. In that case, the thermal properties provided the most significant benefit, allowing processing using less energy. There also appears to be benefit in recycling graphene-PET nano-composites over other additives in the recycle stream. Mechanical property enhancement from graphene nanocomposites remains the most important benefit for manufacturing.

The promise of graphene nanocomposites to provide the lightweight high performance alternative to 20<sup>th</sup> century materials still stands. However, adaptation of nanocomposites in day-to-day applications outside the laboratory at industrial scale are lagging due to limitations with dispersing the nano-phase. A new approach of dosing nano-phase materials dispersed in a liquid medium during industry compatible molding processes can deliver the intended level of property improvements. This new method and resulting property improvements are discussed with examples including: improved thermal conductivity from graphene dispersed through melt mixing and liquid dosing; exfoliated graphene obtained through liquid dispersion improving the elastic modulus without impacting film clarity; and methods to track dosing consistency or quantifying dispersion level. These all indicate an effective exfoliation fraction exists which improves the composite properties.

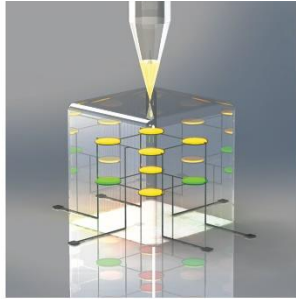
## 3D PRINTING FUNCTIONAL COMPOSITES & DEVICES

Michael C. McAlpine  
Kuhrmeyer Family Chair Professor  
University of Minnesota  
Department of Mechanical Engineering

Key Words: 3D Printing, Nanocomposites, Functional Materials, 3D Printed Electronics, Biomedical Devices



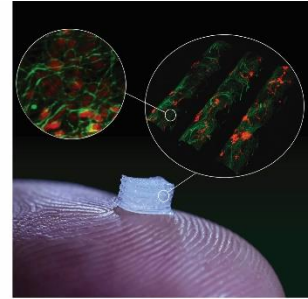
Bionic Organs



3D Electronics



4D Bioprinting



Biomedical Devices

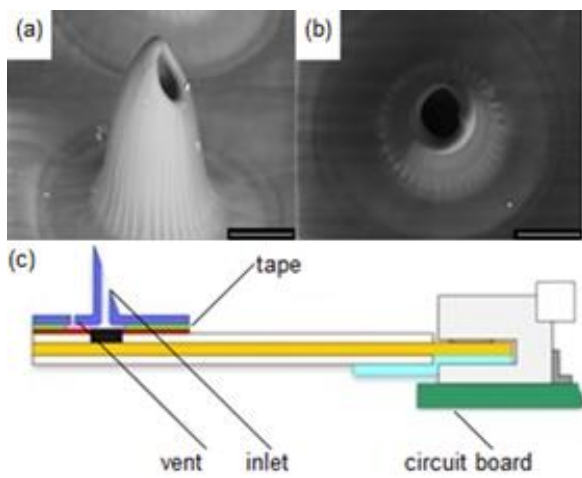
The ability to three-dimensionally interweave biological and functional materials into 3D composites could enable the creation of devices possessing unique and compelling geometries, properties, and functionalities. Interfacing active devices with biology in 3D could impact a variety of fields, including regenerative bioelectronics, smart prosthetics, biomedical devices, and human-machine interfaces. Biology, from the molecular scale of DNA and proteins, to the macroscopic scale of tissues and organs, is three-dimensional, soft and stretchable, and temperature sensitive. This renders most biological platforms incompatible with the fabrication and materials processing methods that have been developed and optimized for functional electronics, which are typically planar, rigid and brittle. A number of strategies have been developed to overcome these dichotomies. Our approach is to use extrusion-based multi-material 3D printing, which is an additive manufacturing technology that offers freeform, autonomous fabrication. This approach addresses the dichotomies presented above by (1) using 3D printing and imaging for personalized, multifunctional composite architectures; (2) employing 'nano-inks' as an enabling route for introducing diverse functionality; and (3) 3D printing a range of functional inks to enable the interweaving of a diverse palette of materials into devices, from biomedical to electronic. 3D printing is a multiscale platform, allowing for the incorporation of functional nanoscale inks, the printing of microscale features, and ultimately the creation of macroscale devices. This blending of 3D printing, functional composites, and 'living' platforms may enable next-generation 3D printed devices, all dispensed from a one-pot printer.

# **ADDITIVE MANUFACTURING OF INORGANIC-ORGANIC HYBRID MATERIALS FOR TRANSDERMAL BIOSENSOR APPLICATIONS**

Roger Narayan, North Carolina State University  
rjnaraya@ncsu.edu

Key Words: additive manufacturing, biosensor, microneedle, inorganic-organic hybrid material

Two photon polymerization offers many advantages over conventional processes for scalable mass production of medical devices, particularly those with small-scale features. First, the raw materials (e.g., inorganic-organic hybrid materials and acrylate-based polymers) used in two photon polymerization are inexpensive and are widely available. Second, two photon polymerization can be established in a conventional “dirty” manufacturing environment; no cleanroom facilities are required. Third, two photon polymerization is a straightforward and single-step process for creating complex structures with small-scale features. In previous work, two photon polymerization was shown to be able to create microneedles with a larger range of shapes and dimensions than conventional microneedle fabrication techniques [1]. For example, 500-700 micrometer tall microneedles were created out of an acrylate-based polymer that is used in Class IIa medical devices (e.g., hearing aid shells) (Figure 1 (a) and Figure 1 (b)) [1]. A hollow microneedle was used to create pores in the outermost layer of cadaveric porcine skin; a microneedle-generated pore was shown to facilitate delivery of carboxyl quantum dots to the deep epidermis and dermis layers of the cadaveric porcine skin within fifteen minutes. We have prepared several types of hollow microneedle-based biosensors using microneedles that were fabricated using either two photon polymerization or digital micromirror device-based stereolithography. In these biosensors, the sensing mechanisms are located within the bores of the microneedles. For example, we have examined incorporating carbon fiber electrodes within a hollow microneedle array, which was created using a digital micromirror device-based stereolithography instrument [2]. Studies involving trypan blue dye demonstrated that the microneedles remained intact after they punctured the outermost layer of cadaveric porcine skin. The carbon fibers were chemically modified to allow for the detection of hydrogen peroxide and ascorbic acid; the performance of the microneedle-based sensors was demonstrated using electrochemical measurements. In another study, we prepared a multiplexed microneedle-based biosensor array for simultaneous and selective amperometric detection of lactate, glucose, and pH over physiologically relevant analyte levels in complex media (Figure 1c) [3]. In another study, a solid-state ion selective electrode for potassium ions was prepared from three-dimensional porous carbon [4]. This electrode was integrated with a hollow microneedle that was created using two photon polymerization. The functionality of the ion selective electrode was demonstrated over the physiologic range of potassium and in the presence of interfering sodium ions.



*Figure 1. (a, b) Scanning electron microscopy images that were obtained from an acrylate-based polymer microneedle, which was prepared using two photon polymerization. Scale bar=100  $\mu$ m. From Reference 1. (c) Schematic showing design of the multicomponent microneedle-based biosensor platform. From Reference 4.*

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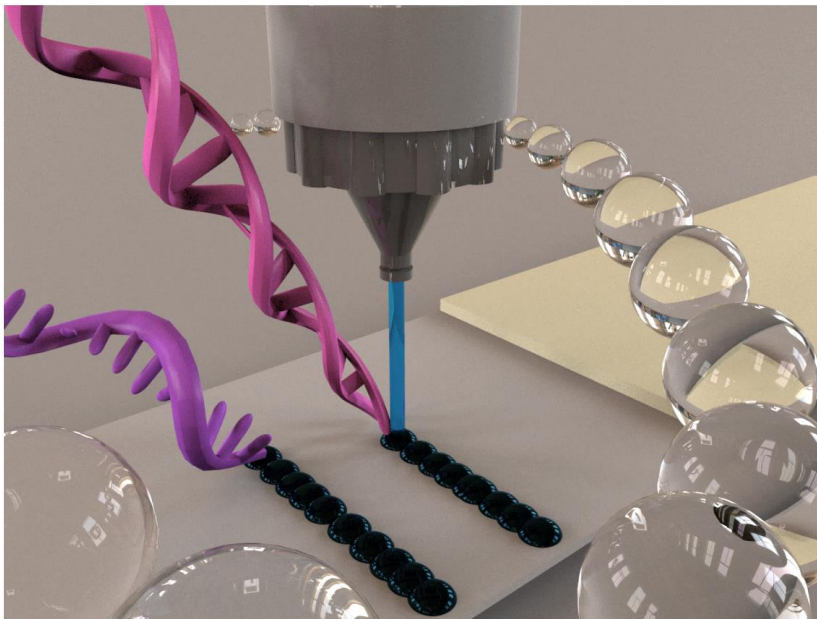
## BIO - NANOPATTERNING: INKJET PRINTED NANOPATTERNED APTAMER - BASED SENSORS FOR IMPROVED OPTICAL DETECTION OF FOODBORNE PATHOGENS

Lia Stanciu, Materials Engineering, Purdue University  
lstanciu@purdue.edu

Susana Diaz, Materials Engineering, Purdue University

**Key Words:** aptasensors, biopatterning, ink-jet printing; pathogen detection

The increasing incidence of infectious outbreaks from contaminated food and water supplies continues to impose a global burden for public health. There is a market demand for on- site, disposable, easy- to- use, and cost- efficient pathogen sensing devices. Despite the rapid growth of biosensing as a research field, and the generation of breakthrough technologies, more than 80% of the biosensors developed at the laboratory scale never will get to meet the market. This work presents a cost- efficient, reliable, and repeatable aptasensing platform for the whole-cell detection of foodborne pathogens in real food samples. An optimized inkjet printing platform was designed, taking advantage of the carefully controlled bionanopatterning of novel carboxyl- functionalized aptameric inks on a nitrocellulose substrate. The



aptasensors demonstrated a highly efficient detection of whole-cell *E. coli* O157:H7 ( $10^1$  colony forming units (CFU)  $\text{mL}^{-1}$  in pure culture and  $10^2$  CFU  $\text{mL}^{-1}$  in ground beef), with no need for cell lysis. This sensing platform has a controlled sensing response variation within  $\pm 1$  SD for at least 75% of the data collected even at very low concentrations. To the best of the authors' knowledge, this work reports the lowest limit of detection of a paper- based whole- cell optical sensor for *E. coli* O157:H7, with enough evidence to prove its high repeatability, as well as specificity at genus, species, strain, and serotype level.



## PEROVSKITE NITRIDES: A NEW PLAYGROUND FOR FUNCTIONAL MATERIALS

Geoff Brennecke, Colorado School of Mines

geoff.brennecke@mines.edu

Kevin Talley, Colorado School of Mines

Rachel Sherbondy, Colorado School of Mines

Andriy Zakutayev, National Renewable Energy Laboratory

Key Words: Perovskite, Nitride, Piezoelectric, Semiconductor, Ferroelectric

The perovskite crystal is a favorite playground for electroceramists across a wide variety of applications, and recent developments on hybrid metallorganic perovskite photovoltaics has renewed interest in expanding the chemical space of this flexible and multifunctional crystal structure. A survey of experimentally confirmed simple perovskite compounds ( $ABX_3$ ) finds no reports of pure  $X=N$  anion chemistries. One challenge of forming nitride perovskite materials is the high valence cations needed to satisfy the high valency of nitrogen; another is limiting oxygen impurities. Computational predictions of energetically favorable nitride perovskites have been reported<sup>[1]</sup> and DFT+LDA methods<sup>[2]</sup> suggest that the lowest energy state of  $LaWN_3$  is a non-centrosymmetric  $R3c$  type distorted perovskite structure with a spontaneous polarization of approximately  $60\mu C/cm^2$  along the  $\langle 111 \rangle$  polar axis. A relatively low energy barrier predicted for polarization reversal raises the possibility of ferroelectricity as well. Developing a ferroelectric nitride would greatly simplify integration of a number of functional (e.g., ferroelectric, piezoelectric, and more) properties directly with nitride semiconductors for a variety of integrated sensing and energy conversion applications. Here we report the experimental confirmation of oxygen-free  $LaWN_3$  as a perovskite (Fig. 1) using multiple fabrication approaches. Calculations show 5 different symmetries with very similar lattice energies (3 polar and 2 non-polar); refinements of x-ray and electron diffraction in conjunction with property measurements document the complexity of the  $LaWN_3$  system in addition to other closely-related perovskite nitrides.

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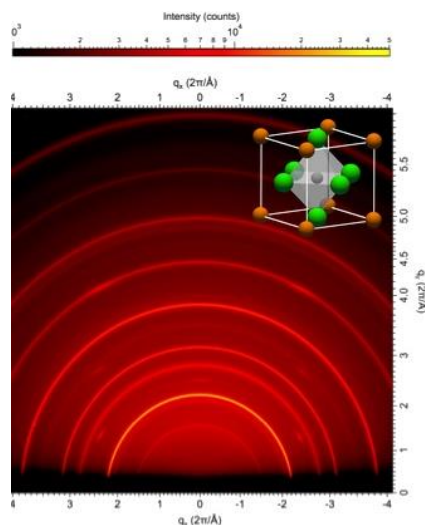


Figure 17 – Diffraction pattern confirming fabrication of the first-reported nitride piezoelectric,  $LaWN_3$ .

# AG NANOWIRE-BASED NANOCOMPOSITES FOR INTERCONNECTS OF FLEXIBLE/WEARABLE ELECTRONICS

Byungil Hwang, School of Integrative Engineering, Chung-Ang University, Seoul, 06974, Republic of Korea  
E-mail: bihwang@cau.ac.kr

Key Words: Ag nanowire, nanocomposite, interconnect, flexible, wearable.

With the recent increasing interest in wearable/stretchable electronics, there are concentrated efforts to develop a material system for flexible/stretchable interconnects that can endure severe mechanical deformations. The most widely used strategy to fabricate stretchable interconnects is to form polymer composites by embedding conductive fillers such as metal particles or metal nanowires into the elastomeric polymer matrix. The conductive fillers can form a percolated network in the polymer matrix, which enables the polymer composites to serve as conductors. Because of the elastomeric properties of the polymer matrix, the composites could withstand mechanical strain while maintaining the conductive properties until the percolation in the network of the conductive fillers is lost below the critical percolation threshold above which conduction can start. The volumetric deformation of the polymer matrix under severe mechanical strain causes disconnection of the percolated network, which results in the degradation of conductivity. Since the loss of percolation is highly dependent on the mechanical properties of the polymer matrix, the development of a stretchable polymer matrix that is high compatible with the conductive fillers is urgently needed.

There are several candidates for the stretchable polymeric matrix such as poly(dimethylsiloxane) (PDMS, and Ecoflex (a type of platinum-catalyzed silicone). PDMS showed a high stretchability of ~200% and good chemical stability, and is thus widely used for substrates of stretchable interconnects. However, solution coating on PDMS is difficult due to its highly hydrophobic surface that required additional surface treatment to modify the surface property, thus limiting its use in multilayer-structured electronic devices. Ecoflex is the emerging material for stretchable electronics and is known to withstand a tensile strain of more than 700%. In addition, the ease of tuning the colors from transparent to saturated colors as well as its biodegradable characteristic makes it an attractive candidate for wearable electronics. However, the large elastic mismatch of Ecoflex with other organic/inorganic materials used in electronics adversely affects the reliability of devices that require moderate stretchability. Different polymers show different mechanical and chemical properties; thus, selecting an appropriate polymer matrix for specific applications is key to the development of stretchable electronics. In this regard, increasing the available material options for the stretchable polymer matrix is necessary, especially for wearable electronics that have a large variety of applications and these applications determine the required properties of the materials used for each device. For example, the polymer strip for wristbands needs a relatively higher modulus than that for the electronic devices applied to elbows. However, the choice for stretchable polymer-matrix materials used for stretchable interconnects is limited.

In this study, we explored the application of a trimethylolpropane formal acrylate (TFA)-based polymer matrix as a potential candidate stretchable substrate for stretchable electronics. The UV-cured TFA films were highly transparent and were able to withstand a tensile strain of ~100% (Figure 1), which is suitable for wearable electronics where the human motion generates ~75% strain. To show the suitability of the TFA films for stretchable interconnects, Ag nanowires were embedded on the surface of the TFA films using a well-known peeling off process. The efficient transfer of the Ag nanowires to the polymer matrix is important to prepare highly transparent and conductive stretchable interconnects. For this, special treatments such as the self-assembled monolayer (SAM) treatment is typically required to change the surface of the base substrate hydrophobically. However, with the TFA resin, the Ag nanowires could be successfully transferred from the glass substrate without a special surface treatment, which enabled easy fabrication and cost reduction. In addition, the elastomeric TFA matrix was attachable to polymeric substrates such as polyethylene terephthalate (PET) and glass substrates, which make it a promising candidate material for the substrates of patchable devices. Such possible applicability of TFA for stretchable substrates was systematically studied by characterizing the optical, electrical, and mechanical properties, which are presented in this paper. In addition, the potential application of the stretchable supercapacitor using the TFA/Ag nanowire interconnects as the current collector is demonstrated.

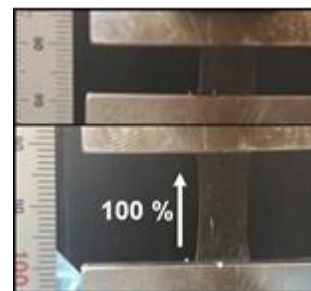


Figure 1 Photo of tensile test of TFA/Ag nanowire composite

## SELF-STRENGTHENING POLYMER BY VIBRATION

Aaron Esser-Kahn, The University of Chicago  
aesserkahn@uchicago.edu  
Zhao Wang, The University of Chicago  
Jun Wang, The University of Chicago

Key Words: mechanochemistry; thiol-ene; self-strengthening; organogel; piezo-sensing;

Materials in everyday use are subjected various conditions, temperature, humidity and more particularly mechanical vibration. Though rational designs have been made to withstand these environmental effects, materials still become weaker overtime under cyclic loading. In nature, bone cells can adapt to cyclic loading by adding bone accordingly, a process called bone remodeling. This endows bone the ability to strengthen when subjected to stresses thereby preventing structural damage and improving the mechanical strength. Inspired by this, we have previously demonstrated the strengthening of material by ultrasound triggered polymerization and polymer crosslinking but lack adaptive nature to different loadings, particularly for the low frequency vibration (<20kHz) that material usually suffered. Herein, we describe a bone-remodeling-mimic strategy to harnessing low frequency vibration energy (500-5000Hz) and use for strengthening material. We used piezoelectric ZnO nanoparticle to mechanochemically initiate thiol-ene “click” reaction in an organogel system. The organogel can sense and adapt accordingly to the input vibrational energy, in terms of power, time and frequency, showing a maximum 60 times increase in modulus. Moreover, the degree of adaption can be monitored and self-reported to external electronics driven by its change in modulus. This integration of programable feature enables the precise control of material's property for a wide range of applications.

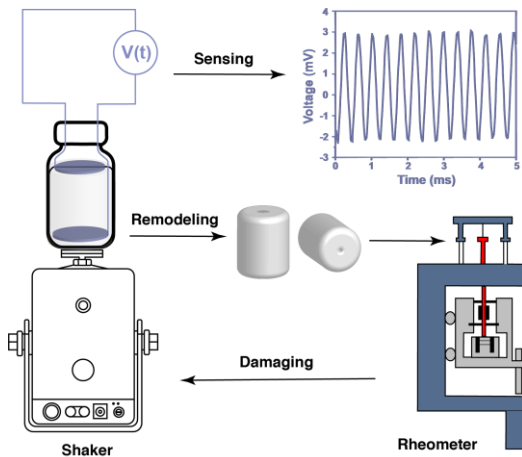


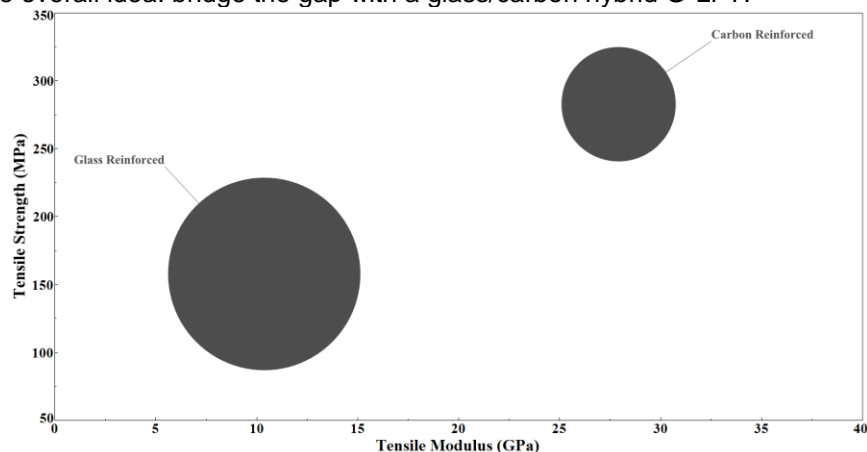
Figure 18 – Representation of sensing and remodeling of self-strengthening polymer by vibration

# DEVELOPMENT AND OPTIMIZATION OF HYBRIDIZED GLASS/CARBON LFT COMPOSITES FOR COST AND PERFORMANCE

Kristin Nicole Hardin, Nippon Electric Glass  
Kristin.Hardin@neg-us.com  
Nathan Bergler, PlastiComp  
Jacob Anderson, Northrop Grumman

**Key Words:** Hybrid, Long Fiber Thermoplastics, Performance Optimization, Performance Modeling, Design of Experiments

Long glass fiber has been in the industry for many years in a variety of applications ranging from nonstructural initially, to semi-structural now. However, the sticking point in this is that in many of these applications performance requirements aren't being reached by the glass fibers where they're either not strong enough, stiff enough, or some subset of the above. Thus, more performance is needed for those applications. A lot of the times this scenario leads to the question why not go to carbon fiber? Many industries like aerospace and sporting goods go this route because carbon fiber is lightweight and has much higher stiffness and strength than glass fibers. In many cases that stiffness and strength is too great. It's more than the application requires, but there's really not a material system that can bridge the gap between the performance criteria. This results in over designing the component. That's one negative. Another is, it's very expensive. This really summarizes the problem. Figure 1 shows the "G-LFT landscape" that gives a survey of materials, readily available on the web, where the various properties were combined to create this bubble plot. Between the properties of glass reinforced and carbon reinforced composites is a large gap in performance. If an application requires performance here, in order for it to use a composite solution you have to go up to carbon fiber, which again, is cost prohibitive. And you can't go to glass fiber because it won't meet the performance needs. A new question arises: why can't we hybridize the two and form a bridge from the glass fiber reinforcement performance to the carbon fiber reinforced plastics performance? For this particular scenario were looking at G-LFT but this approach could be applied to other material systems. In the case of G-LFT the question arises, can we develop a tailored product for a given application and maximize the cost and performance ratio and make it economically justifiable. Thus, the overall idea: bridge the gap with a glass/carbon hybrid G-LFT.



*Figure 1 – "G-LFT Landscape" showing glass reinforced and carbon reinforced composite properties and the gap that presents an opportunity for the design of glass/carbon hybrids.*

In product development, a lot of times the part is designed based on material performance. In this work a paradigm shift occurs in the concept of developing products for a given application. The first thing is to start with the application and the part itself. Identify the desirable requirements for that part. Run those requirements through a performance and optimization tool. Produce the compound and then validate the performance. If the performance doesn't meet targets, regurgitate information back into a do-loop here until targets are hit. Application requirements can be determined and the compound can be made and tested but the novel part of this work is the optimization tool itself. This work will go through the scientific approach taken to develop this optimization tool that was comprised of several trials and a large DOE. This work shows the validation of the model and presents a case study. This optimization tool allows an OEM to set a price point, density constraints, and allows "fine tuning" of mechanical properties without over designing the part.

## CARBON OXIDATION OVER SILVER/PEROVSKITE-TYPE OXIDE COMPOSITE CATALYSTS

Hidehiko Yahiro, Graduate School of Science and Engineering, Ehime University, Japan  
hyahiro@ehime-u.ac.jp

Key Words: Catalytic Oxidation, Carbon, Perovskite-type Oxide, Silver, Cyano Complex.

The removal of particulate matter (PM) is successively developed as a new catalytic process for the environmental protect. Up to date, silver-loaded ceria ( $\text{Ag/CeO}_2$ ) catalyst has been reported to be the potential catalyst for the removal of PM [1]. However, little is known about the catalytic activity of Ag-loaded perovskite-type oxide for PM oxidation although it has been reported that  $\text{La}_{1-x}\text{Sr}_x\text{CoO}_3$  and  $\text{LaFeO}_3$  catalysts are active for PM oxidation [2]. In the present study, the catalytic activity over silver-perovskite-type oxide composite catalyst such as  $\text{Ag/LaFeO}_3$  and  $\text{Ag/LaCoO}_3$  etc. was examined for the oxidation of carbon as a model compound of PM. The catalysts were prepared by two different methods: a conventional impregnation method with silver nitrate solution on perovskite-type oxide (Method I) and a thermal decomposition of heteronuclear cyano-complex adsorbing Ag ions (Method II) to yield Ag-loaded perovskite-type oxide composite catalysts [3, 4].

Figure 1 shows the carbon oxidation activity ( $\text{CO}_2$  concentration) over  $\text{Ag/LaFeO}_3$  catalysts prepared by Methods I and II as a function of temperature. No or less promotive effect of Ag addition on the catalytic activity was observed for carbon oxidation of perovskite-type oxide prepared by Method I. On the other hand, Method II was significantly effective for enhancing the catalytic activity of carbon oxidation. The catalytic activity of  $\text{Ag/LaFeO}_3$  prepared by Method II was comparable to that of  $\text{Ag/CeO}_2$  which has been considered to be the potential candidate for PM oxidation. FE-SEM measurements demonstrated that  $\text{Ag/LaFeO}_3$  prepared by Method II provided high dispersion state of Ag particles, compared with  $\text{Ag/LaFeO}_3$  prepared by Method I.

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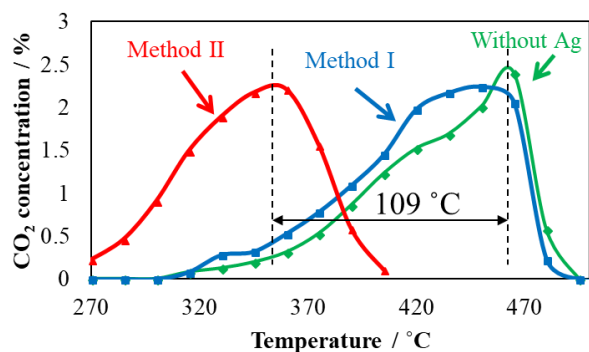


Figure 1. TPR profiles of  $\text{Ag/LaFeO}_3$  catalysts prepared by Method I and II and  $\text{LaFeO}_3$  without Ag loading.

## **BEYOND NANOSILICA: GEOPOLYMERIC NANOALUMINOSILICATES FOR FUNCTIONAL NANOCOMPOSITES**

Dong-Kyun Seo, Arizona State University  
dseo@asu.edu

Shaojiang Chen, Arizona State University  
Wenwen Zhang, Arizona State University

**Key Words:** Geopolymer, Nanozeolites, Sustainability, Aluminosilicates, Nanocomposites

Nanoaggregates such as nanosilica and carbon black are two of the most important inorganic nanomaterials used in modern technologies including nanocomposites. By using sustainable geopolymer chemistry, we introduce new aluminosilicate nanoaggregates and nanostructured zeolites which may become as important as the aforementioned materials in nanocomposites, with their own unique functionalities. Geopolymer has been extensively studied and utilized as “green cement” in addressing global warming issues, one of the most challenging problems in human sustainability. At the same time, it is one of the few inorganic material systems that can be produced in a large scale and thus has a potential to meet the demand of large-scale applications. We will describe the nature of the sustainable, scalable production methods and discuss the key features of the materials including morphologies, surface areas, porosity, aggregate size, and zeolitic crystallinity. The nanostructured zeolite products demonstrate the “nano” effect of their own, in terms of the short diffusion lengths within individual crystals and of the high surface area. Examples of their superior performances will be given for their applications in their neat form. Expansion of the original synthetic method has allowed organic-modified nanoaluminosilicates with increased hydrophobicity which can be important in nanocomposite fabrication.



## IN SITU SYNCHROTRON STUDIES OF OXIDE CERAMICS TO 3,000°C

Waltraud M. Kriven, University of Illinois at Urbana-Champaign, USA  
kriven@illinois.edu

A quadrupole halogen lamp furnace (QLF) capable of heating to 2,000°C in air has been developed in our laboratory, in collaboration with Dr. Julius Schneider at the Ludwig Maximilian University in München, Germany. A conical nozzle levitator (CNL) developed by Dr. Richard Weber at Materials Modification in Chicago, Illinois is capable of in situ XRD measurements of oxides to 3,000°C in air. These two instruments were used at the Advanced Photon Sources (APS) at the Argonne National Laboratory, and the QLF was used at the National Synchrotron Light Source II (NSLSII) at Brookhaven National Laboratory to carry out the following experiments:

- (i) Thermal expansion measurements in 3-D
- (ii) Solid state phase transformations
- (iii) Solid state chemical reactions
- (iv) In situ determination of phase diagrams

A variety of ceramic and mineral examples are provided to illustrate the seven crystal systems (cubic, tetragonal, orthorhombic, rhombohedral, hexagonal, monoclinic and triclinic). Computer software (Program CTEAS) has been developed to visualize the thermal evolution in 3D for individual {hkl} planes, principle strain directions and whether they are increasing or decreasing. When a crystal undergoes a phase transformation upon heating, the 3D crystal structural, lattice correspondence between the parent and product phases can be identified from the continuity of thermal expansion for planes in the parent phase which approximately “become” planes in the product phase. The example is given of a peritectic reaction in the binary  $\text{HfO}_2\text{-Ta}_2\text{O}_5$  system where  $\text{Hf}_6\text{Ta}_2\text{O}_{17}$  decomposes on heating into liquid  $\text{HfO}_2\text{-Ta}_2\text{O}_5$  solid solution plus  $\text{HfO}_2$  at  $2242 \pm 16^\circ\text{C}$ . A  $Z = 4$ , pseudo-subcell is identified which is common to the parent and product phases, which, coupled with vector analysis identifies a lattice correspondence between them, and hence possible orientation relationship.

The oxidation of SiC dispersed into  $\text{ZrB}_2$  was studied as an example of a solid state reaction where the kinetics and chemical mechanisms were elucidated. Intermediate crystalline phases that were formed during oxidation of  $\text{ZrB}_2$ , could be identified and quantified in real time. The oxidation of  $\text{ZrB}_2$  phase could be followed independently of concurrent phases, whether amorphous or crystalline, or simultaneous reactions. Increasing the SiC content in the  $\text{ZrB}_2\text{-SiC}$  composites retarded the oxidation of  $\text{ZrB}_2$ . A novel approach to estimate the thickness of an oxidation layer formed during oxidation of  $\text{ZrB}_2$  and  $\text{ZrB}_2\text{-SiC}$  composites, in-situ at high temperatures was proposed, based on fractional conversion of  $\text{ZrB}_2$  to  $\text{ZrO}_2$ .

A systematic approach to the rapid production of the high temperature, ternary  $\text{HfO}_2\text{-Ta}_2\text{O}_5\text{-TiO}_2$  phase diagrams is presented. This study highlights the combined use of: (i) in-situ high temperature X-ray diffraction on heating to 2,000°C in the QLF, as well as on cooling of liquids from 3000 °C in air in the CNL, and (ii) extraction of common atomic motifs with associated material symmetry analysis. The  $\text{HfO}_2\text{-Ta}_2\text{O}_5\text{-TiO}_2$  ternary phase diagram has 4 congruently melting compounds:  $\text{HfO}_2$ ,  $\text{Ta}_2\text{O}_5$ ,  $\text{TiO}_2$  and  $\text{TiTa}_2\text{O}_7$  and 2 incongruently melting compounds:  $\text{Hf}_6\text{Ta}_2\text{O}_{17}$  and  $\text{HfTiO}_4$ . There are no ternary congruently melting compounds. Symmetry relations between  $\text{Hf}_6\text{Ta}_2\text{O}_{17}$  and  $\text{HfTiO}_4$  have been identified. Symmetry decomposition shows that these two structures are simply related to each other via polyhedral rotations. Finally, 10 invariant reactions were identified in this phase space. There is sufficient in-situ high temperature X-ray diffraction data to analyze the ternary between the lowest melting point isotherm and the room temperature isotherm.

## COHERENT NANOPRECIPITATES WITHIN A BIOGENIC SINGLE CRYSTAL: FROM SPINODAL DECOMPOSITION TO A PRESTRESSING STRATEGY

Boaz Pokroy, Department of Materials Science and Engineering, Technion Israel Institute of Technology  
bpokroy@technion.ac.il

Key Words: biocomposite, prestressed, crystal growth.

We recently discovered a unique biostrategy for strengthening and toughening brittle crystals of calcite [1]. Our studies on the atomic- and nano-structure of the mineralized lenses of the brittle star *Ophiocoma wendtii* revealed the presence of metastable coherent nanoprecipitates that induce compressive stress on the crystal. Although the final nanostructure is akin to the Guinier–Preston (GP) zones well known in classical metallurgy the brittle star achieves this nanostructure via a completely novel mechanism, in which crystals are formed at ambient conditions from a supersaturated amorphous precursor having coherently aligned nanoprecipitates and coherently alternating stress and elastic modulus layers. This induces compressive stress, which strengthens and toughens the mineralized tissue. In this talk I will present our study on the characterization of such crystals utilizing state-of-the-art techniques and will present the most possible mechanism of their formation both in biological and synthetic systems. [2]

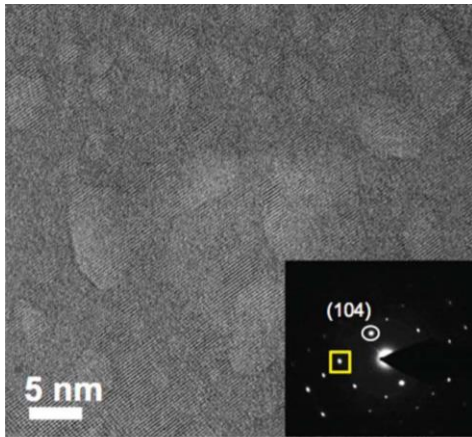


Figure 19 – HRTEM image of a thin section from a lens revealing brighter nanodomains. A lattice image undisrupted by the nanodomains, which demonstrate coherent interfaces with the lattice by the continuous lattice fringes although electron diffraction image (inset) from this area is that of a single crystal.

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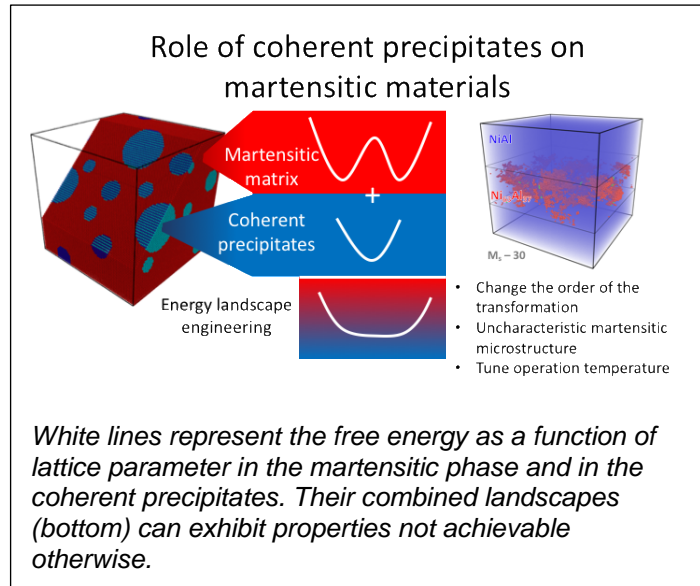
# ROLE OF NANOSCALE COHERENT PRECIPITATES ON THE THERMO-MECHANICAL RESPONSE OF MARTENSITIC MATERIALS

Alejandro Strachan, Purdue University  
[strachan@purdue.edu](mailto:strachan@purdue.edu)

Key Words: molecular dynamics, coherent interface, superlattice, martensitic transformation

Martensitic phase transitions are first order, diffusionless, solid-to-solid, transformations that underlie shape memory, superelasticity, and strengthening in modern steels, impacting a wide range of technologies. While shape memory and superelasticity in traditional alloys are well understood from a mechanistic point of view, recent unexpected results by our group and others indicate a much richer set of phenomena yet to be fully characterized and with significant potential to result in improved or tunable properties. Specifically, martensitic materials with coherent second phases or nanoscale variations in composition have been shown to exhibit uncharacteristic, and some unprecedented, properties.

I will discuss recent work in our group that combines theory with high-fidelity atomistic simulations to demonstrate that a tailored, coherent second phase can modify the free energy landscape that governs the martensitic transformation and achieve notable changes in response, see Figure on the right. We demonstrated that a coherent second phase can reduce the energy barrier that separates the martensite and austenite phases and reduce the hysteresis of the transformation.<sup>1</sup> More importantly, we demonstrated ultra-low stiffness metallic alloys with high strength.<sup>2</sup> We predicted Young's moduli as low as 2 GPa, a value typical of soft materials, in full density metallic nanomaterials. This remarkable result is possible by the stabilization of a thermodynamically unstable state with negative stiffness via interfacial stresses caused by the coherent second phase. MD simulations further revealed how the size and shape of the second phase affects the hysteresis and temperature of the phase transition as well as the martensitic microstructure.<sup>3</sup> In addition, we showed that coherency stresses from an appropriately chosen second phase can also change the nature of the martensitic transformation in metallic alloys from first order (discontinuous transitions) to second order or continuous transformations. Large scale MD simulations showed a remarkable change in the character of the martensitic transformation in Ni-Al alloys near the critical point. We observed continuous transformation, uncharacteristic martensitic microstructures, and scaling behavior described by power-law exponents compatible to those of similar second-order transitions.



<sup>1</sup> Guda Vishnu, K. & Strachan, A. Shape memory metamaterials with tunable thermo-mechanical response via hetero-epitaxial integration: A molecular dynamics study. *J. Appl. Phys.* **113**, 103503 (2013).

<sup>2</sup> Reeve, S. T., Belessiotis-Richards, A. & Strachan, A. Harnessing mechanical instabilities at the nanoscale to achieve ultra-low stiffness metals. *Nat. Commun.* **8**, 1137 (2017).

<sup>3</sup> Reeve, S. T., Guda Vishnu, K., Belessiotis-Richards, A. & Strachan, A. Tunability of martensitic behavior through coherent nanoprecipitates and other nanostructures. *Acta Materialia* **154**, 295-302 (2018).

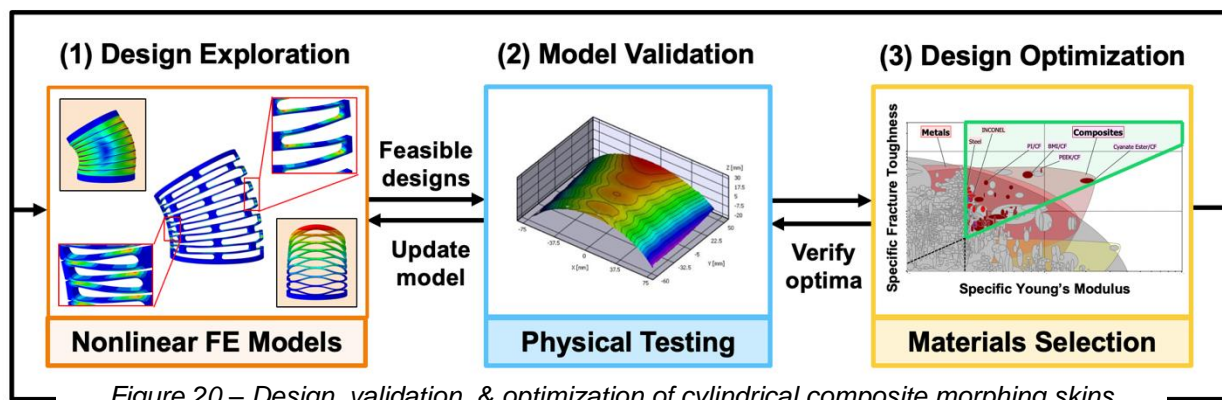
## DESIGN, PRINTING, AND CHARACTERIZATION OF AEROSPACE MORPHING COMPOSITES

Jeffery W. Baur, Air Force Research Laboratory, Materials & Manufacturing Directorate, WPAFB, OH  
Jeffery.Baur@us.af.mil

Wesley Chapkin, Universal Technology Corporation, Beavercreek, OH  
David Seifert, Universal Technology Corporation, Beavercreek, OH  
Patrick Walgren, Texas A&M University, College Station, TX  
Geoff Frank, University of Dayton Research Institute, Dayton, OH

**Key Words:** Morphing, Multifunctional, Topology Optimization, Additive Printing

Multifunctional structural composite are key enablers to future aerospace systems and have the potential to improve mission range and agility without significantly adding weight or reducing internal payload volume. This presentation will discuss efforts to accelerate the design-build-characterize development loop of non-traditional composites using multiphysics design/optimization tools, additive printing of fiber reinforced composites, and in-situ characterization. Previously, multiphysics design/optimization tools were integrated and applied by AFRL for the development of structurally embedded, physically reconfigurable, liquid metal, vascular antennas arrays (SEVA2) with nearly two orders of magnitude modulation in resonant frequency and active thermal management (1). More recently, fiber-reinforced thermosetting printing of structural composites with 90% and 66% of the theoretical tensile modulus and strength of a fully aligned fiber composite have been demonstrated (2). Within this presentation, we discuss the extension of these tools to the rapid exploration, fabrication, and characterization of morphing skins that enable large fuselage bending as a means to improve aero efficiency and agility. The majority of previous efforts in the area of morphing skins have focused on the folding, shear, rotation, or extension of wings. We specifically investigate the optimal designs for composite cylinders that balance the out-of-plane rigidity needed to resist aerodynamic load, and the work needed to reversibly articulate the cylinder 25 degrees or more in any direction while maintaining a smooth outer mold line. We explore thousands of designs for more than a dozen archetypes using bio-inspiration, topology optimization, and finite element methods to arrive at a set of non-dominated designs spanning a range of radial rigidity values and works to articulate. To validate modeled results, we fabricate and characterize each archetype and show strong agreement between model predictions and measured response. As part of the optimization, graphical material selection methods are used to identify the top performing material classes from a known database. We then explore the application of the previously printed composites, embedded actuation, and shape memory polymers for the further optimization of the most promising structures. Overall, we apply advanced design, optimization, printing, and testing methods for the accelerated development of previously unexplored multifunctional morphing skin composites.



- (1) "A Liquid Metal-Based Structurally Embedded Vascular Antenna: II. Multiobjective and Parameterized Design Exploration" D. J. Hartl, G. J. Frank, R. J. Malak, J. W. Baur, *Smart Materials Structures*, 26 (2), 025002, (2017).
- (2) "Mechanical Properties of Printed Epoxy-Carbon Fiber Composites" H. A. Pierson, E. Celik, A. Abbott, H. De Jarrette, L. Sierra Gutierrez, K. Johnson, H. Koerner, J. W. Baur, *J. of Experimental Mechanics*, p. 1-15 (2019).