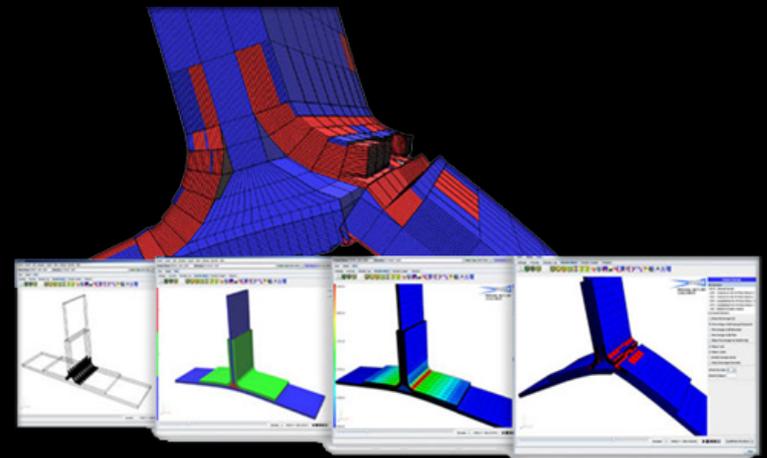


Multifunctional Composites

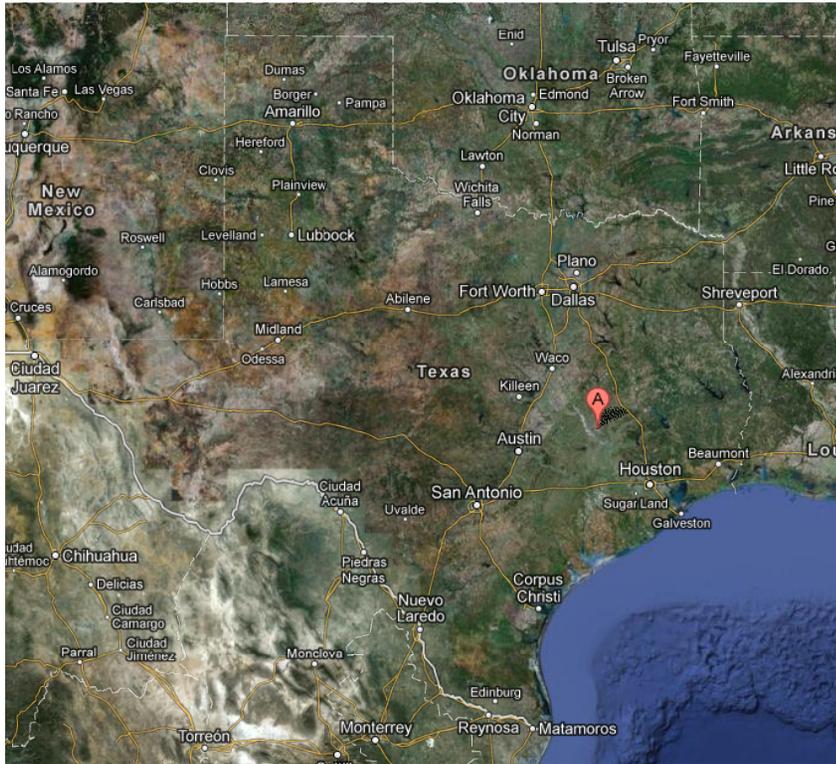
Theocharis Baxevanis

2012 SUMMER SCHOOL IN ADVANCED
COMPOSITE MATERIALS

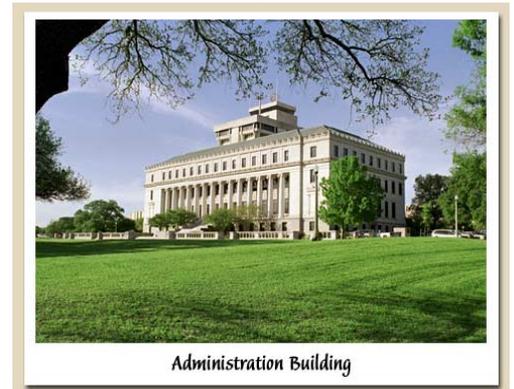
2-6 July



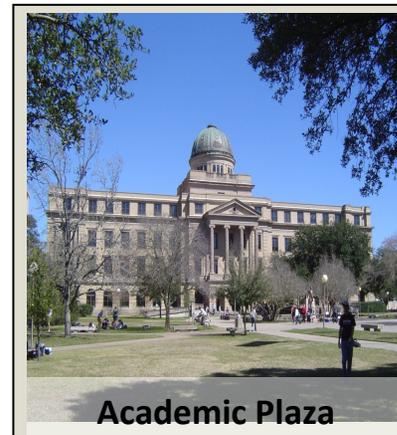
Texas A&M University



Aerospace Engineering



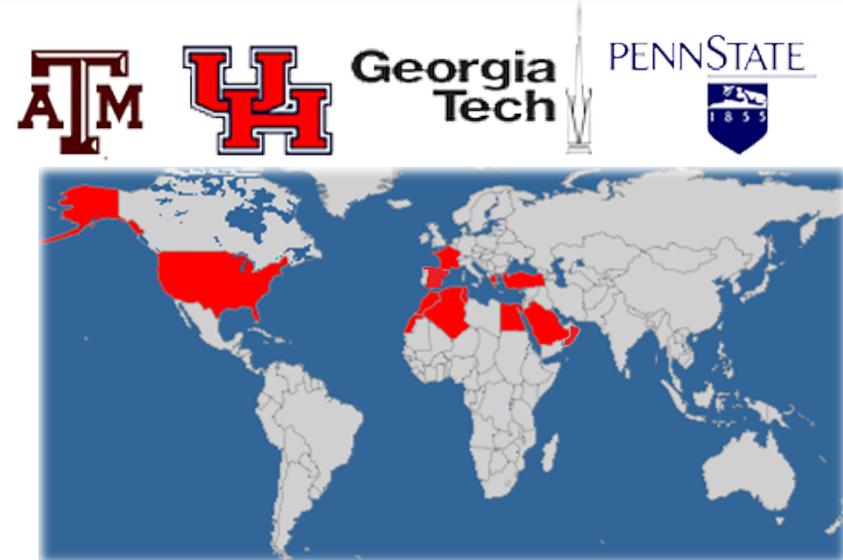
Administration Building



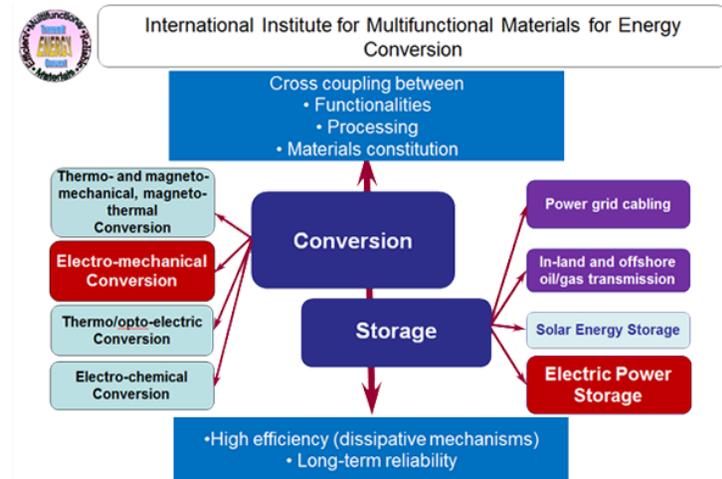
Academic Plaza

IIMEC

- **What is the IIMEC**
The International Institute for Multifunctional Materials for Energy Conversion (IIMEC) is an NSF-funded International Material Institute
- **What is our Mission as a research group?**
The mission of IIMEC is to establish a communications, knowledge-base and computational/laboratory grid that will advance research in multifunctional materials for efficient energy conversion
- **Specific research theme areas:**
 - Coupling of thermal/magnetic and mechanical properties
 - Coupling of electrical and mechanical properties
 - Thermal and electrical, and optical and electrical coupling

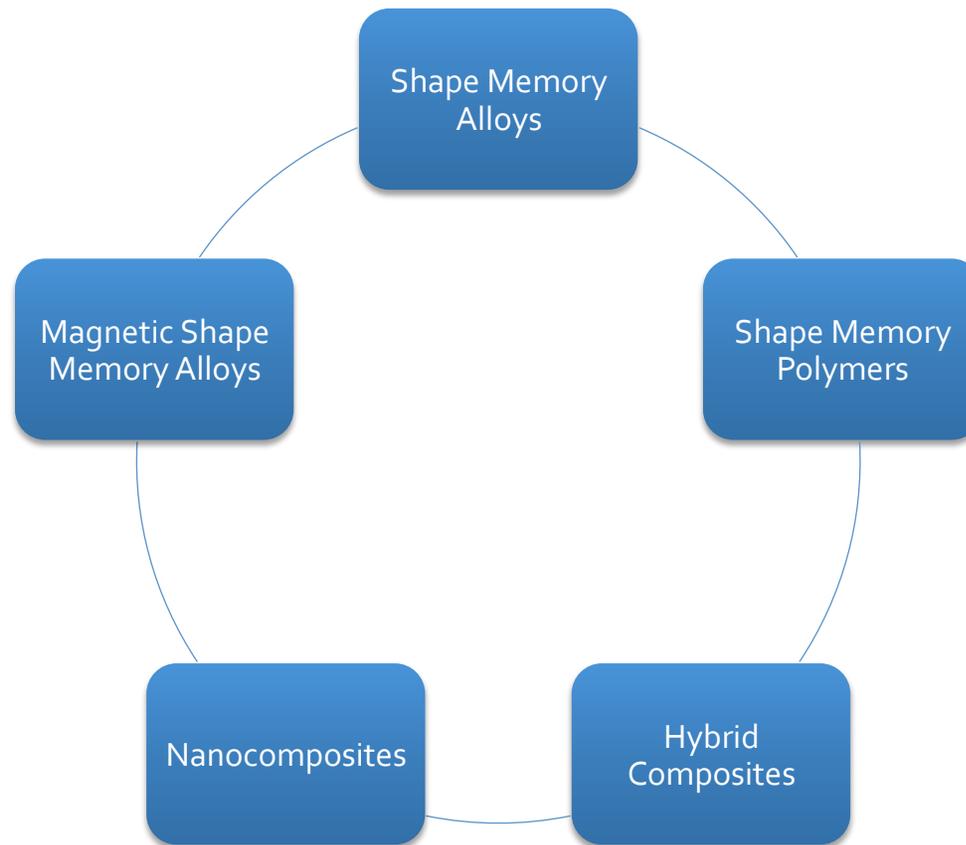


Participating Universities in US and worldwide



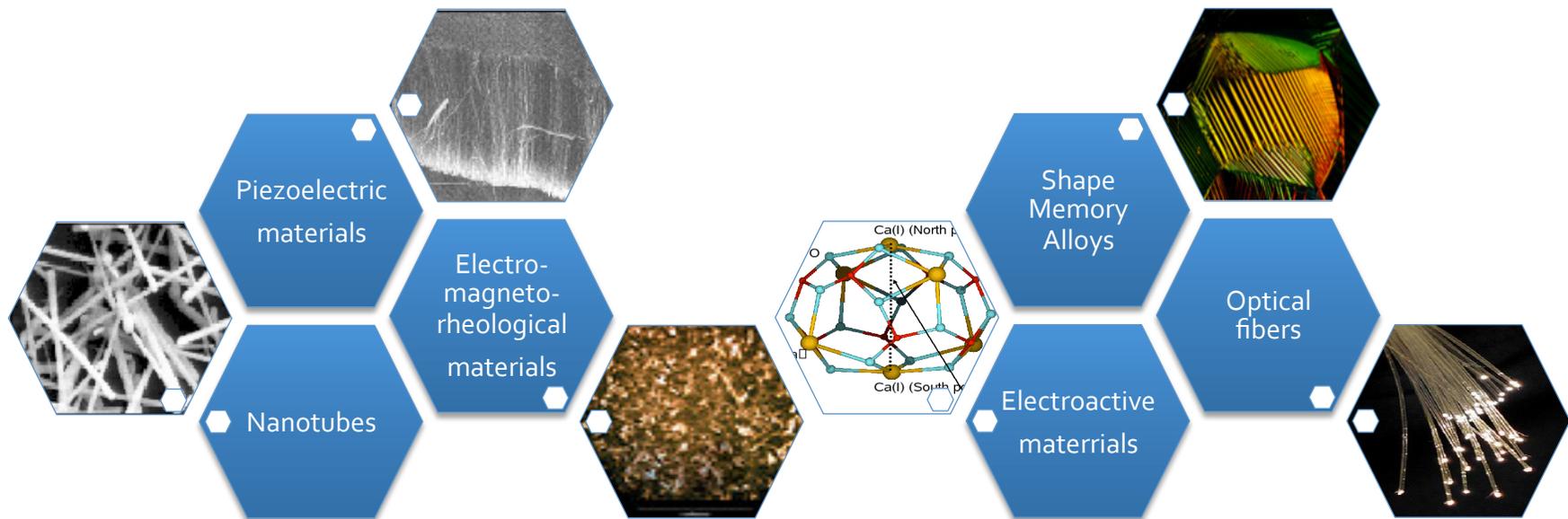
Research in our Group

Characterization, model development, and analysis of



What are Multifunctional Composites?

- Multifunctional Composites are structural materials with added functionality, e.g., energy absorption, electromagnetic properties, sensing and actuation, power harvesting and repair.
- Development of Multifunctional Composites involves the integration of active and passive material systems, often including the coupling of relevant mechanical, electrical, magnetic, thermal, optical, or other physical properties
- Active materials include piezoelectrics, electrostrictives, magnetostrictives, electroactive polymers (EAPs), shape memory alloys (SMAs), shape memory polymers (SMPs) and magnetic shape memory alloys (MSMAs)

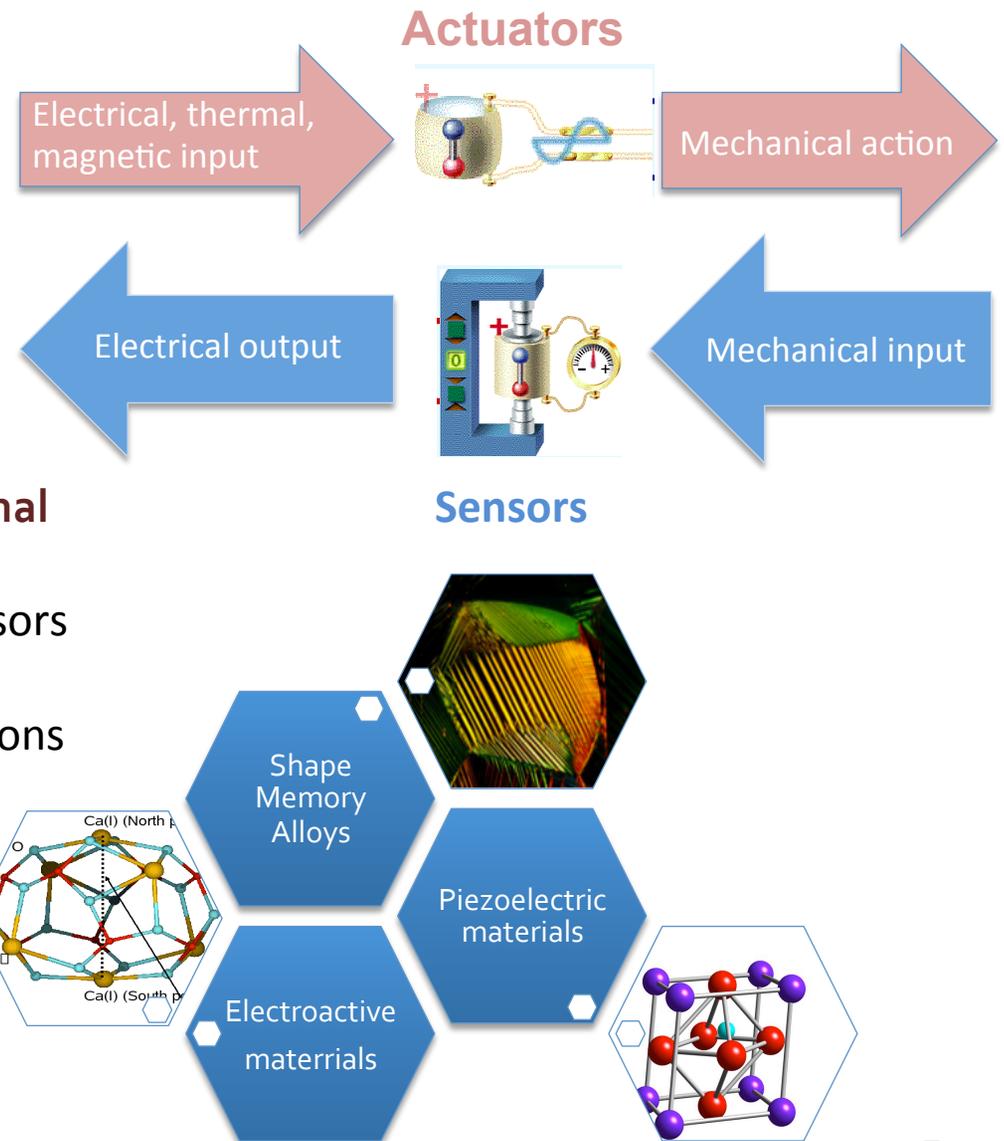


Active Materials

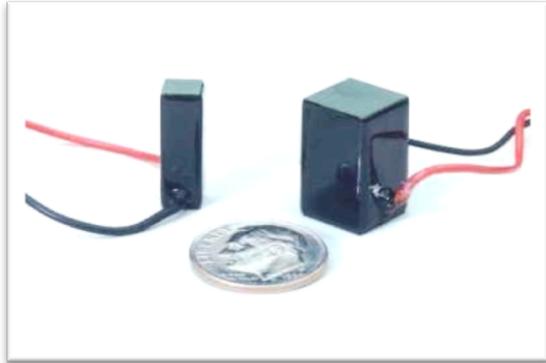
Active materials are able to modify their functional characteristics if stimulated with electrical or magnetic fields, temperature, light, etc...

Main advantages with respect to traditional components:

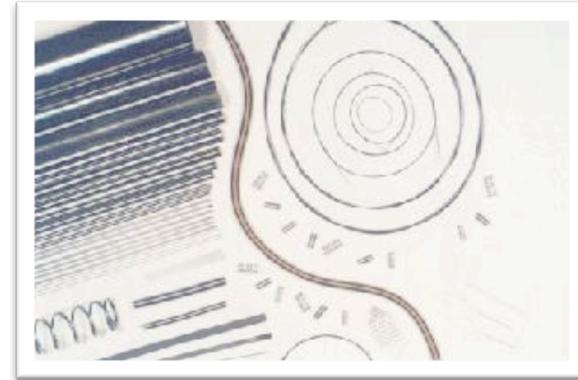
- Act simultaneously as actuators and sensors
- Perform controlled mechanical action
- Are adaptive with environmental conditions
- High level of miniaturization



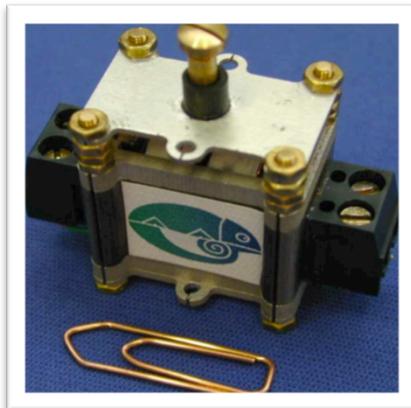
Types of Coupling in Active Materials



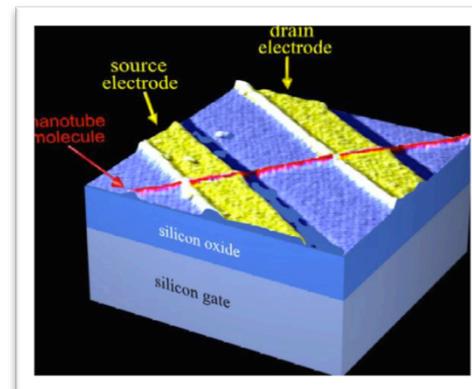
Piezoelectrical Polymers and Ceramics:
Electromechanical coupling



Shape memory alloys:
Thermomechanical coupling

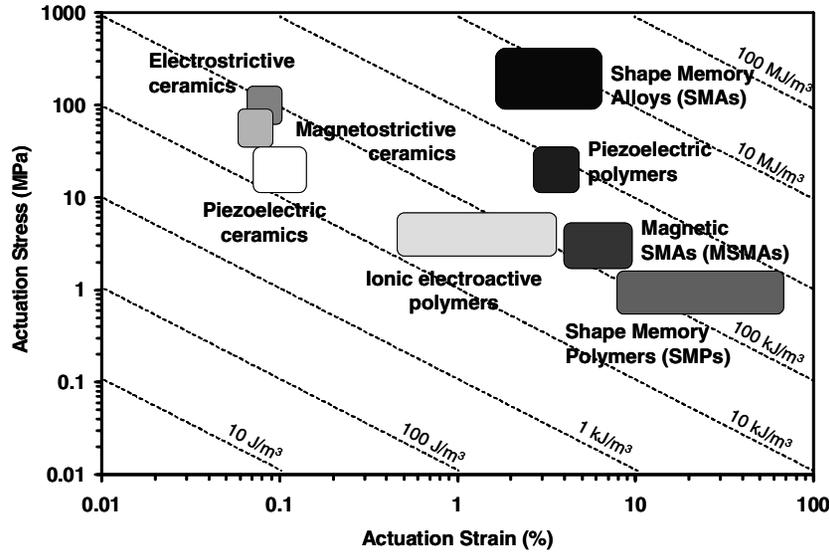


Magnetic shape memory alloys:
Magnetomechanical coupling

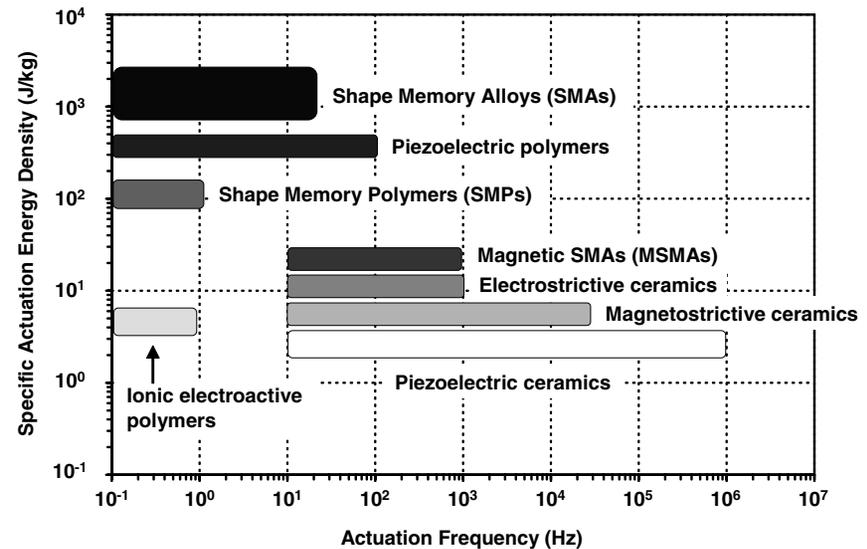


CNT-based devices:
Electrothermal coupling

Mechanical Response of Active Materials

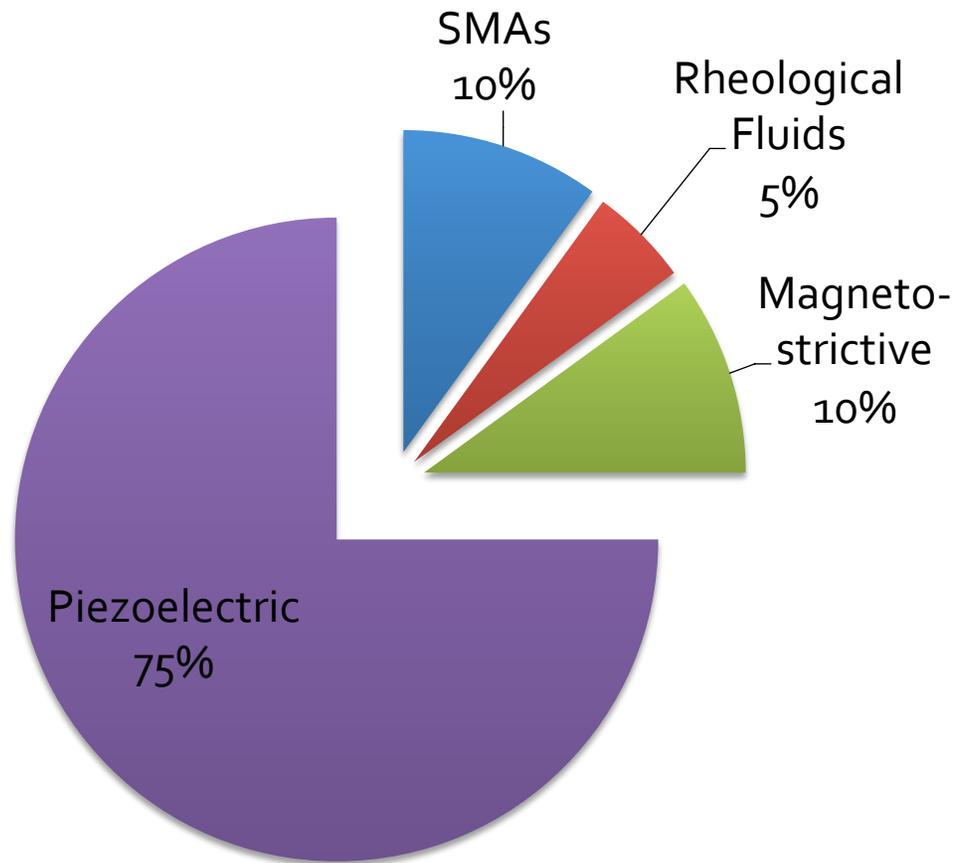


actuation energy density



actuation frequency

Active Materials Market Share



excludes Fiber Optic

Shape Memory Alloys (SMAs)

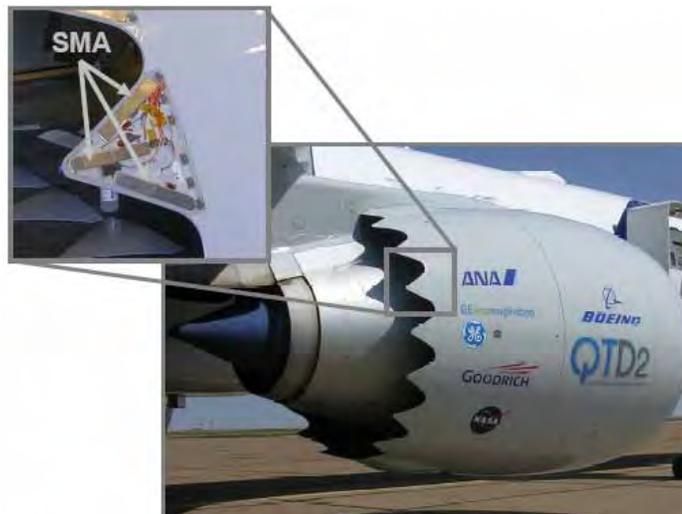
- Shape Memory Alloys (SMAs) are active materials, capable of converting thermal to mechanical work and *vice versa*
- SMAs are desirable in a wide range of actuator, energy absorption and vibration damping applications

Advantages:

- ◆ High Strength
- ◆ High Strain
- ◆ High Actuation Energy

Disadvantages:

- ◆ Low Frequency
- ◆ Low Efficiency



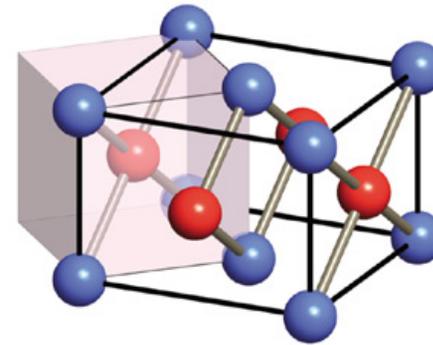
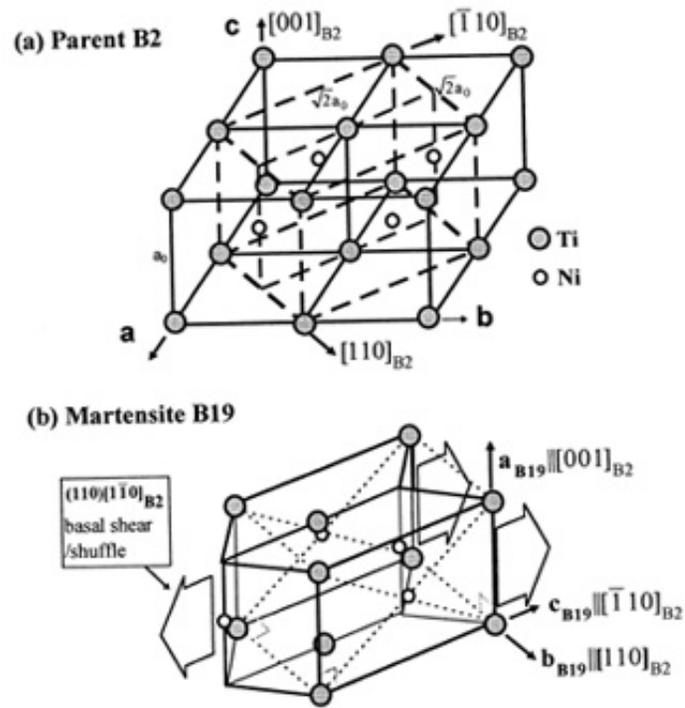
Variable Geometry Chevrons



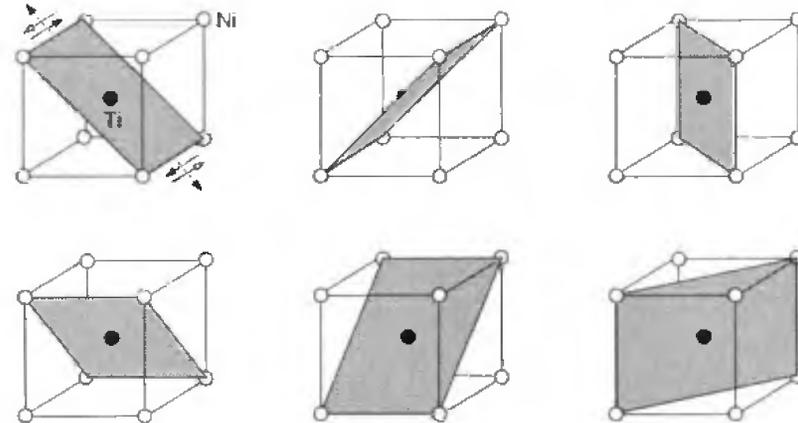
Biomedical devices

Burpee Materials Technology, LLP

Phase Transformation



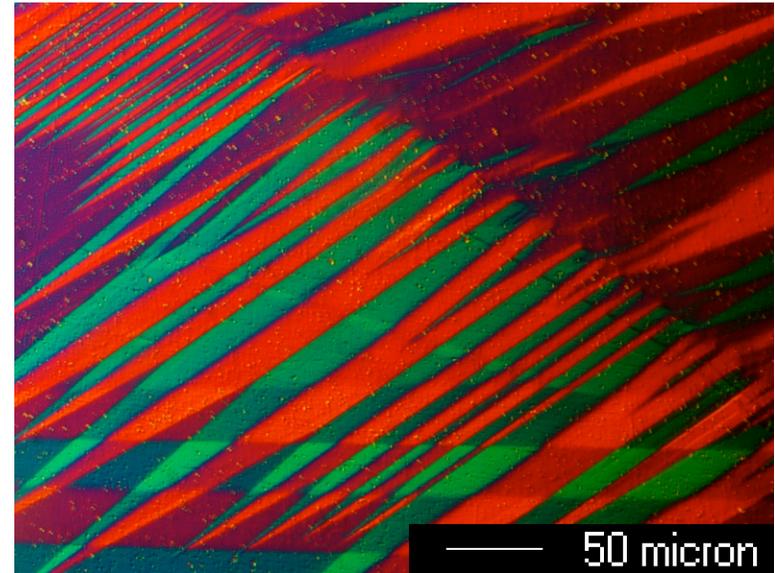
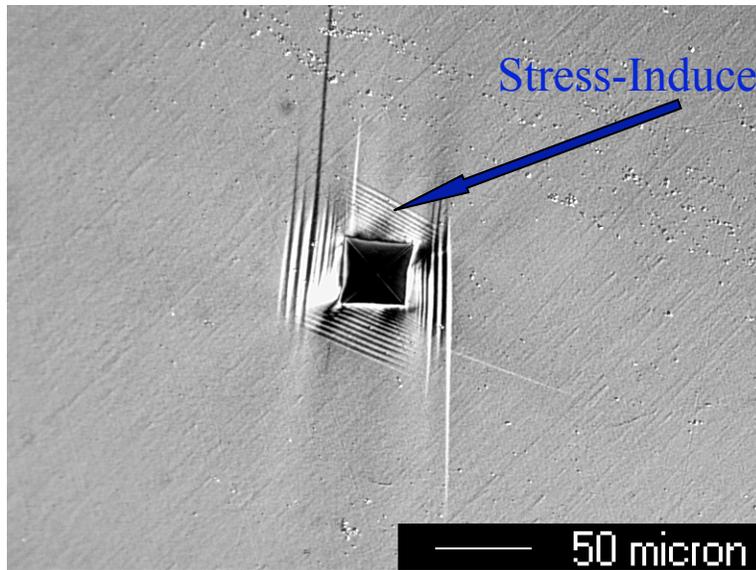
The relation between the cubic B2 cell (shaded box) and the undistorted (tetragonal) B19 cell



Face-diagonal planes. Martensite variants

Diffusionless, shear driven transformation from austenite to martensite and vice-versa

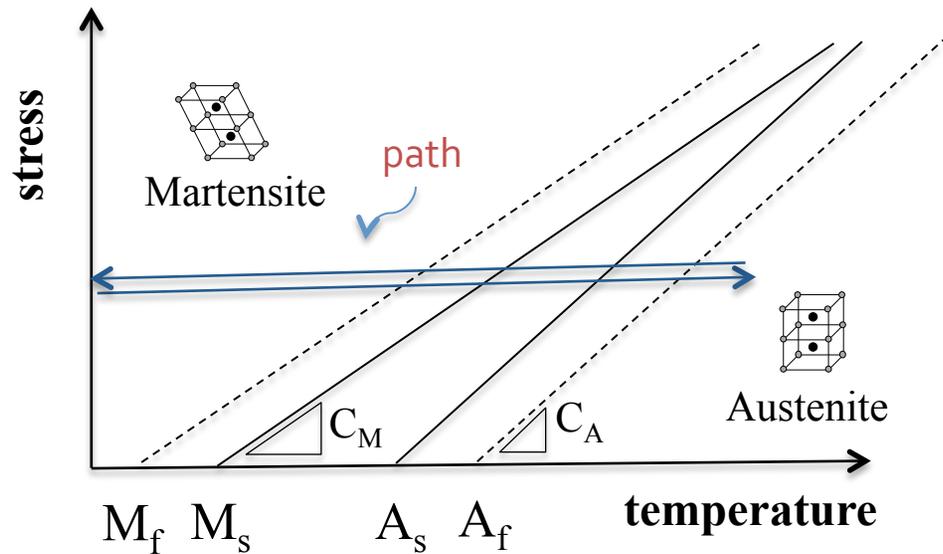
Phase Transformation (cont.)



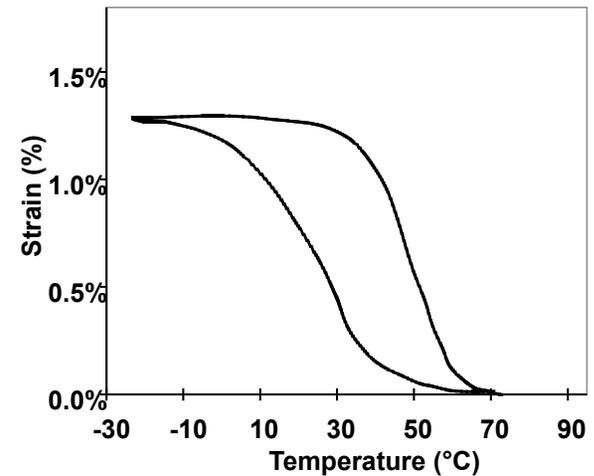
Thermally-Induced martensite

Mechanical Response of SMAs

shape memory effect



stress vs temperature phase diagram



strain vs temperature

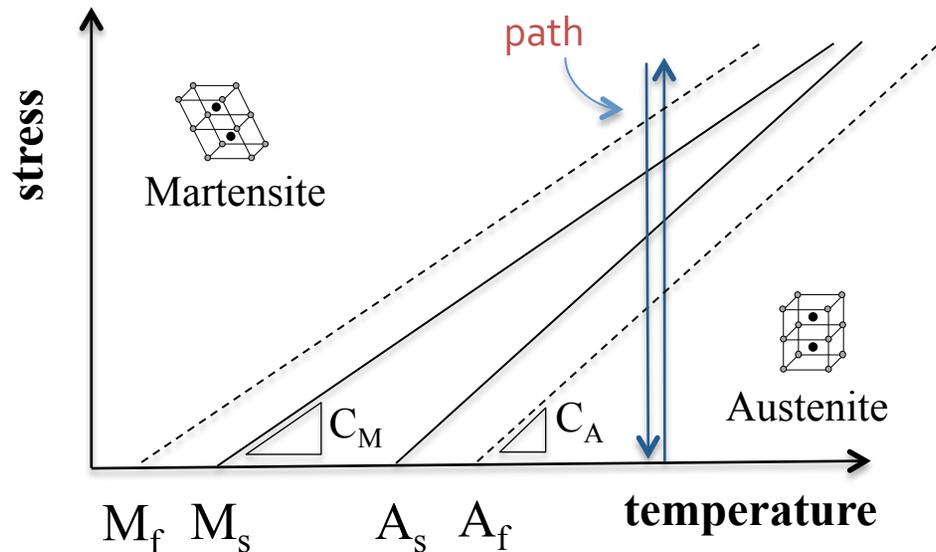
- SMAs can recover their shape when the temperature is increased even under high applied loads (*Shape Memory Effect*)

[Shape memory effect](#)

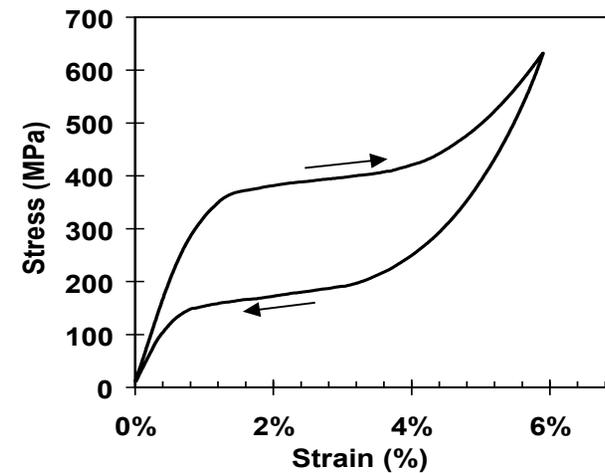
[Pseudoelastic effect](#)

Mechanical Response of SMAs

pseudoelastic behavior



stress vs temperature phase diagram



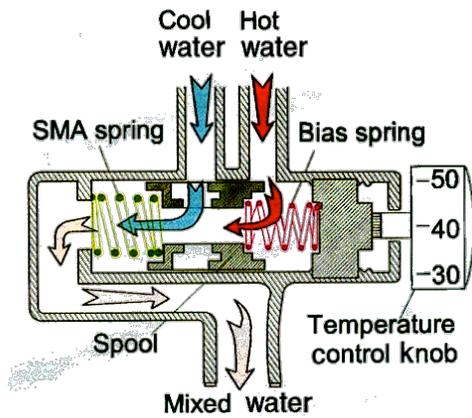
stress vs strain

- Transformation can also be induced by applying a sufficiently high mechanical load to the material in the austenitic phase (*Pseudoelastic Effect*)

[Shape memory effect](#)

[Pseudoelastic effect](#)

Applications

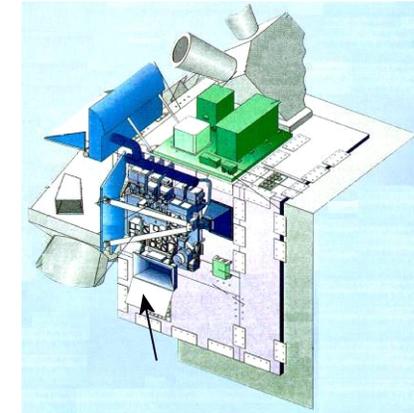


mix

Otsuka (NIMS) 2002

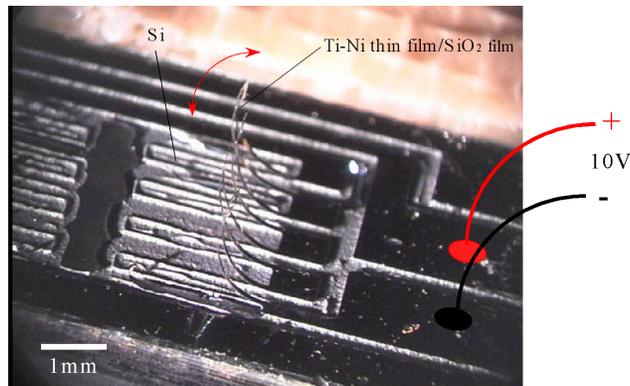


open

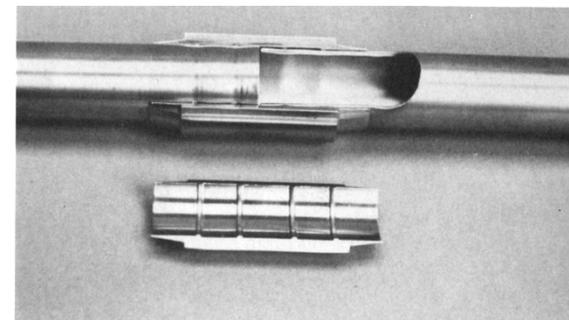


Voggenreiter (EADS) 2001

move

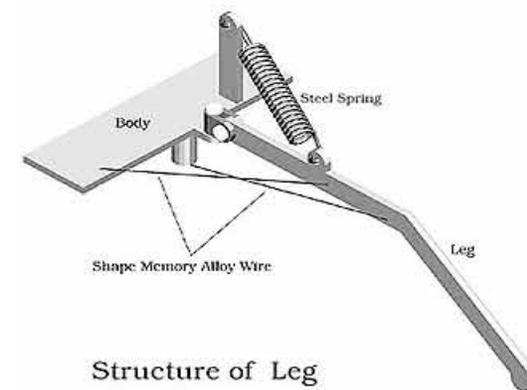
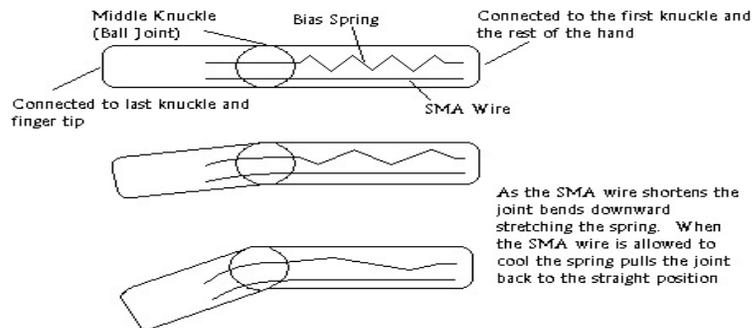
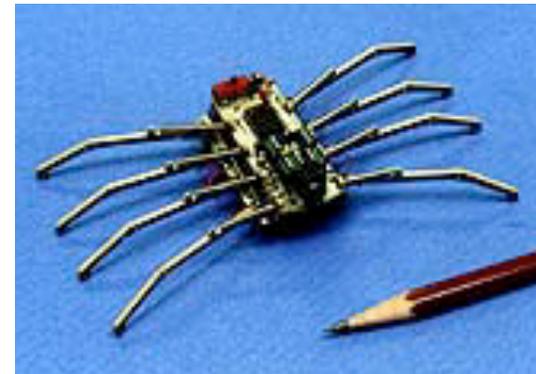


connect



F-14 Raychem 1971

SMA Devices



http://www.cs.ualberta.ca/~database/MEMS/sma_mems/muscle.html

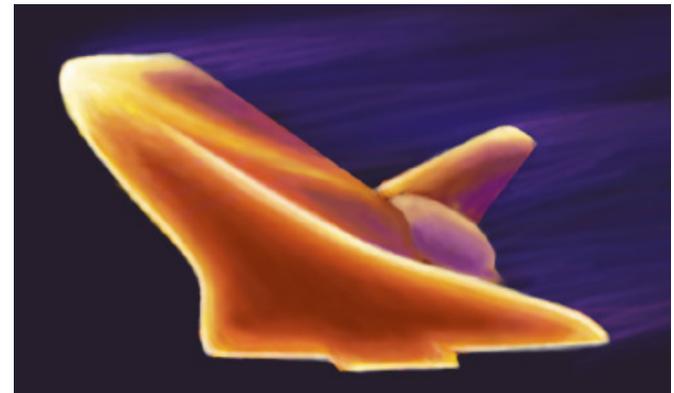
http://www.toki.co.jp/MicroRobot/_8LegRobot.html

An Application...

- Common problem for many aerospace applications:
 - Lack of materials capable of handling extreme environments
 - High Temperature Regimes
- Past solution was metal-ceramic composites
 - Brittleness of ceramics often lead to failure



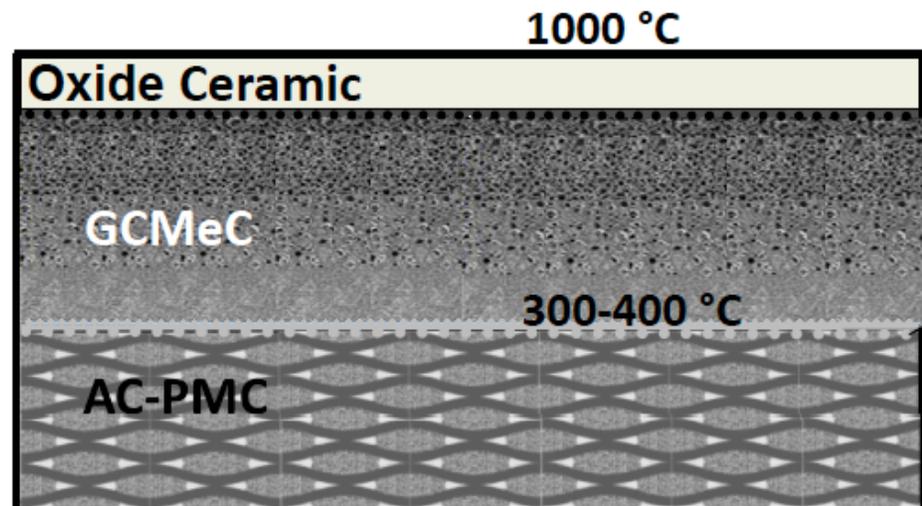
http://en.wikipedia.org/wiki/National_Aerospace_Plane



<http://en.wikipedia.org/wiki/File:Stsheat.jpg>

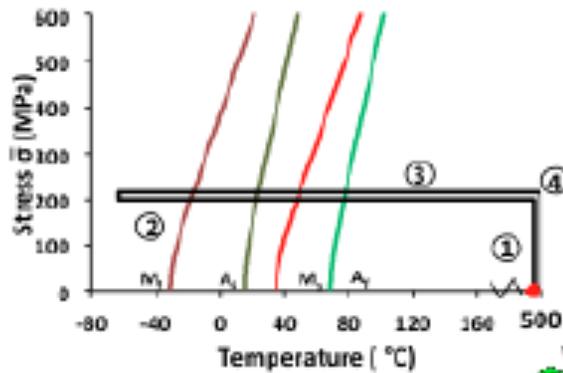
New FG Hybrid Composite

- **New Solution:** New *Functionally Graded Hybrid Composite*
- Top: Oxide Ceramic Thermal Barrier Coating
- Middle: Graded Ceramic-Metal Composite
- Bottom: Actively Cooled Polymer Matrix Composite



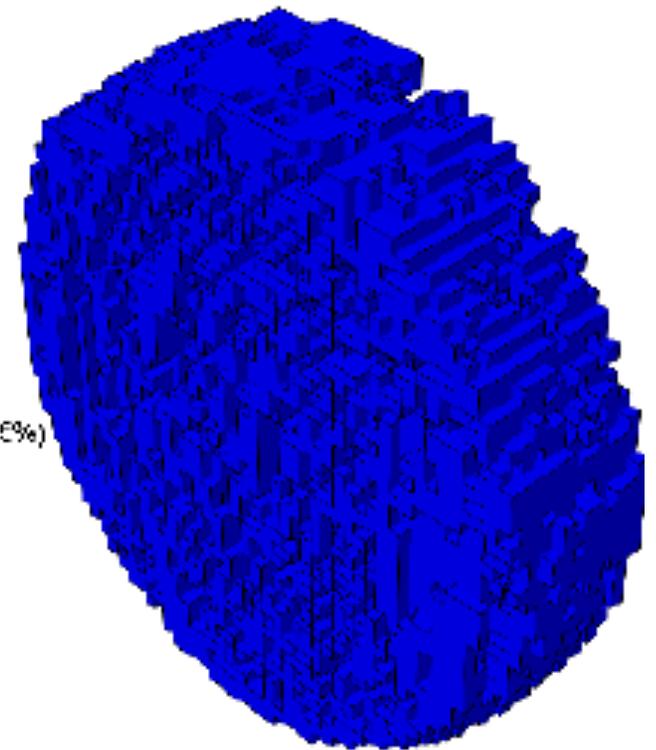
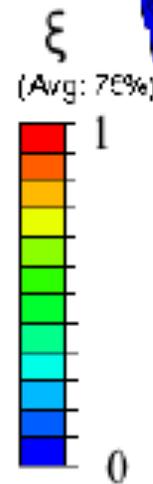
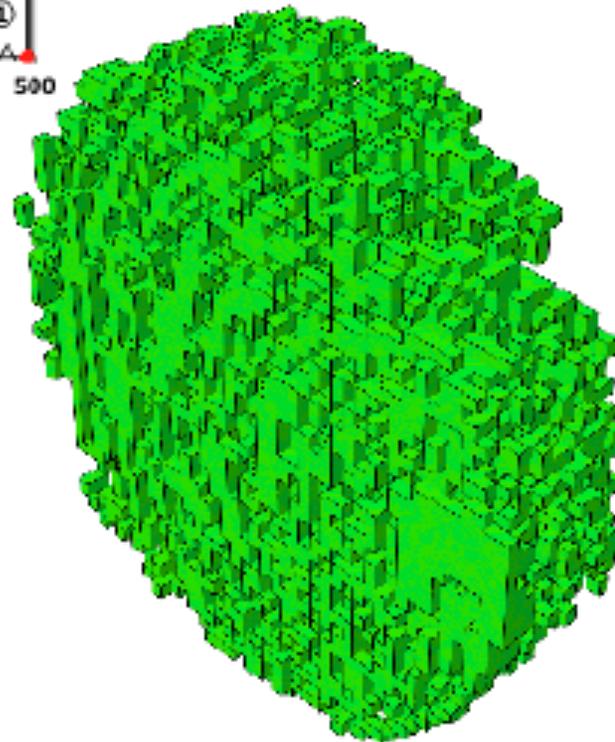
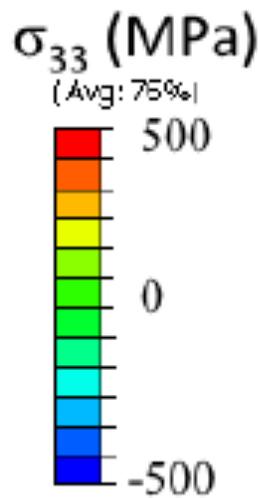
Problem: How to improve mechanical behavior of GCMeC

Ceramic Stress State



Stress in Ceramic Phase

Martensitic Volume Fraction, ξ , in SMA Phase



Shape Memory Polymers

- SMPs present a relatively low-force, high-elongation alternative compared to shape memory alloys (SMAs)
 - Reported strains up to 800% (Liu et al. 2007)
 - Ability to significantly tune material properties
- Potential applications
 - Aerospace devices
 - Biomedical devices



20°C

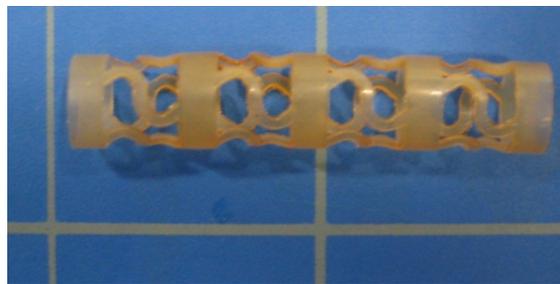
37°C

41°C

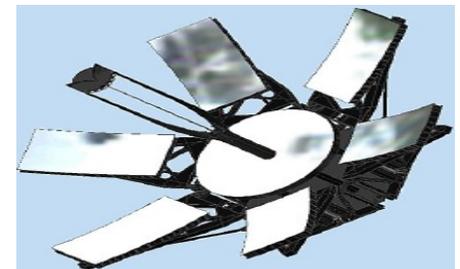
Lendlein and Langer (Science 2002)



Thrombectomy Devices ¹



Cardiovascular Stents ²



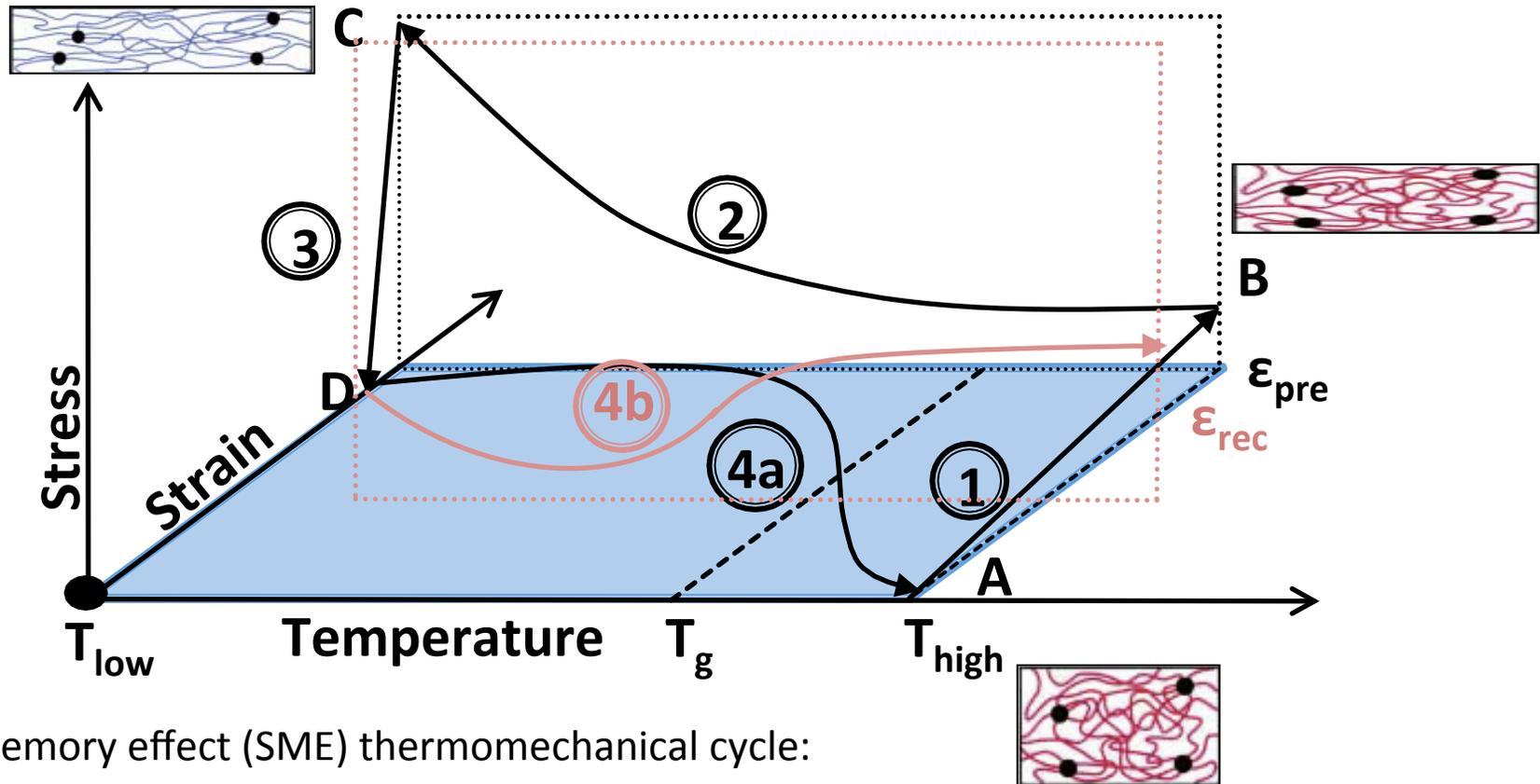
Deployable Space Structures ³

¹Buckley, P.R., et al., *IEEE Transactions on Biomedical Engineering*, 2006.

²Courtesy of Landon Nash

³Lake, M.S., et al., *Proceedings of SPIE*, 1999.

Thermomechanical Cycle

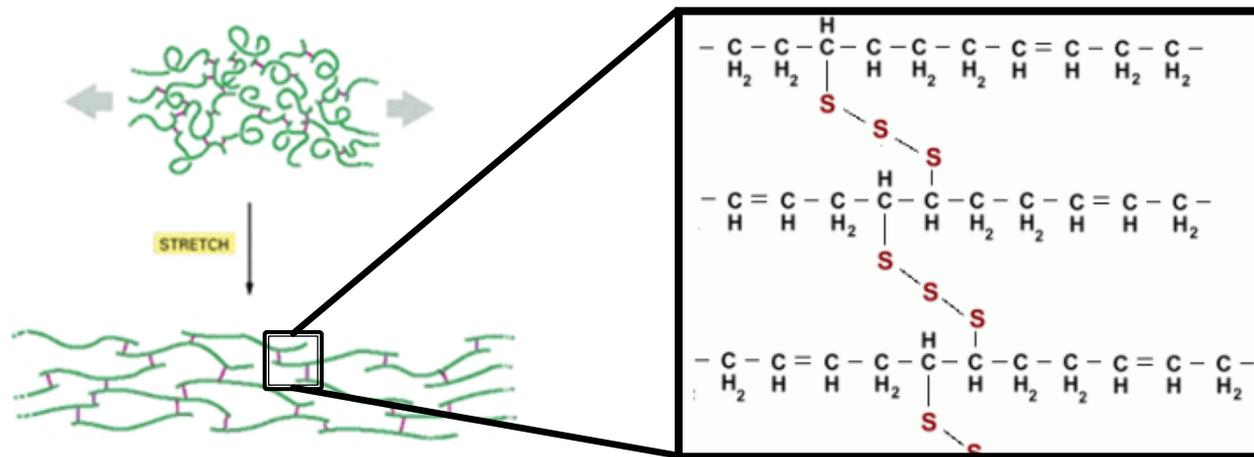


Shape memory effect (SME) thermomechanical cycle:

1. Load in rubbery phase ($T > T_g$)
2. Cool at fixed deformation
3. Unload in glassy phase ($T < T_g$)
- 4a. Free recovery (heat at zero stress)
- 4b. Constrained recovery (heat at constant displacement)

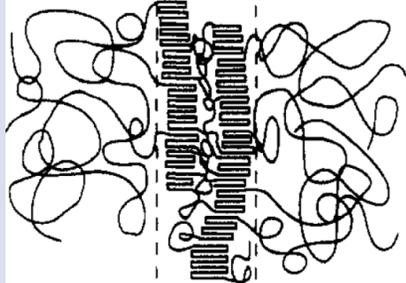
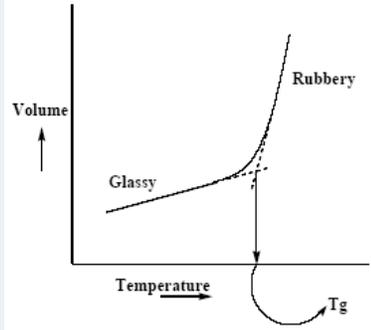
Loading at High Temperature ($T > T_{trans}$)

- Large deformations possible
 - Polyurethane SMPs stretched to 100% strain (Baer et al., 2006; Tobushi et al. 1997)
 - Polystyrene-based SMPs stretched to 75% (Atli et al. 2009) and 100% strain (Volk et al. 2010)
- Deformation mechanism (stretching chains + netpoints) similar to that of stretching vulcanized rubber



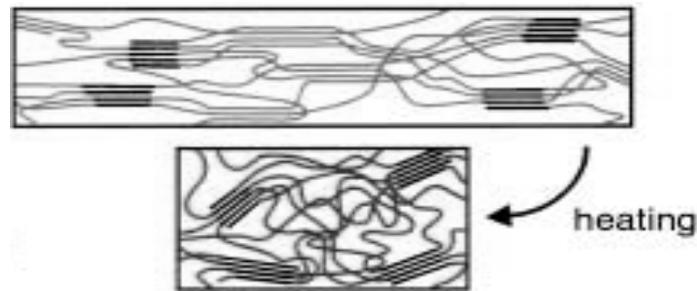
Cooling to $T < T_{trans}$ and Unloading

- 'Freeze' the deformation of the material by cooling while maintaining a constraint (e.g., constant strain)

Type of Switching ('Soft') Segment	'Freezing' Mechanism	
Semi-crystalline $(T_{trans} = T_m)$	Formation of crystalline regions prevents long range motion of amorphous molecules	 <p>Rangarajan et al. (Macromolecules 1998)</p>
Amorphous $(T_{trans} = T_g)$	Transformation from rubber phase to glass phase. Lack of thermal energy results decreases long range motion of molecules.	 <p>(http://www.ejpau.media.pl/)</p>

Recovery at High Temperature ($T > T_{trans}$)

- Heating at zero load to observe shape recovery
 - Stretched polymer chains inherently want to return to their randomly oriented, coiled configurations (entropic gain)



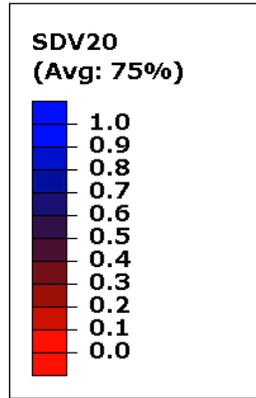
Lendlein and Kelch (Angew Chem. Int. Ed. 2002)

- Thermodynamically consistent:

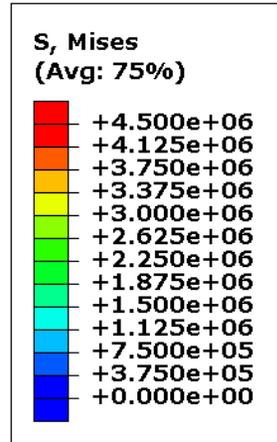
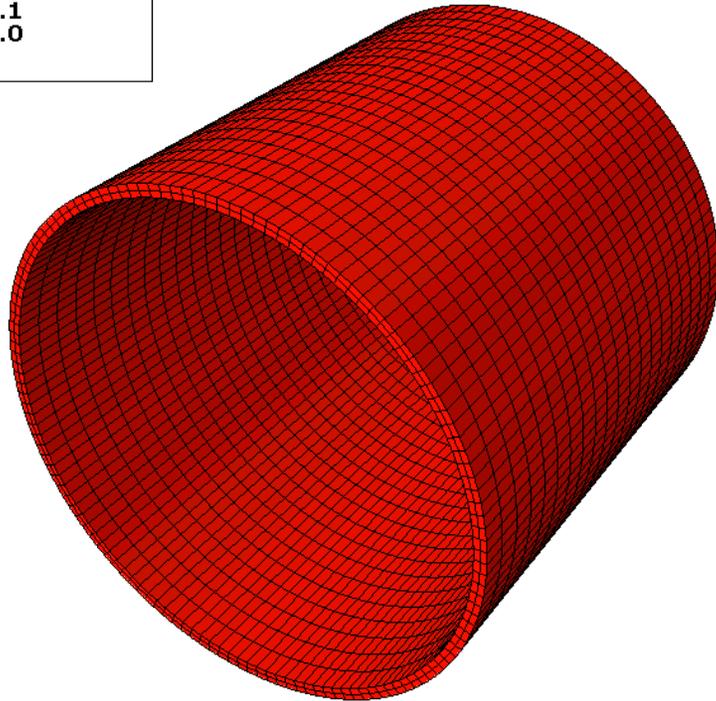
$$\Delta G = \Delta H - T\Delta S$$

Swalin (Thermodynamics of Solids, 1972)

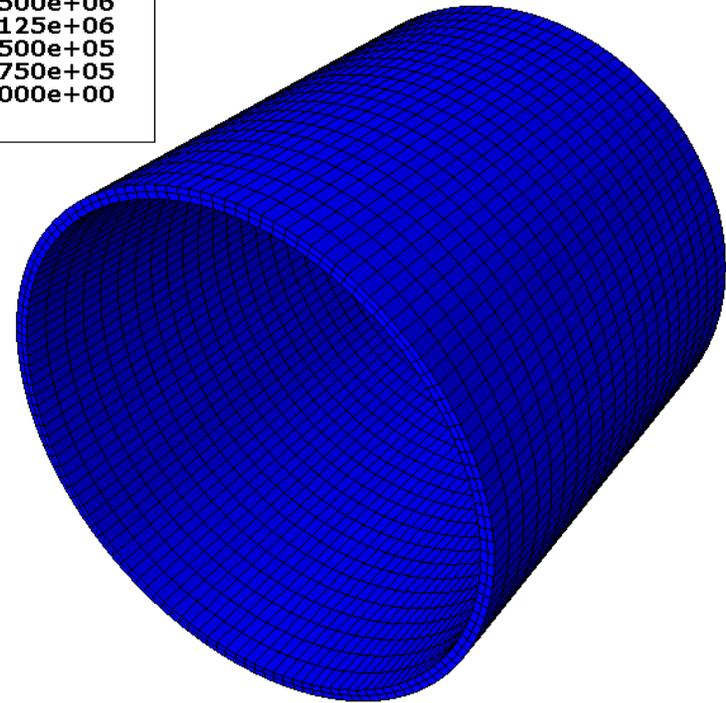
SMP Cardiovascular Tube



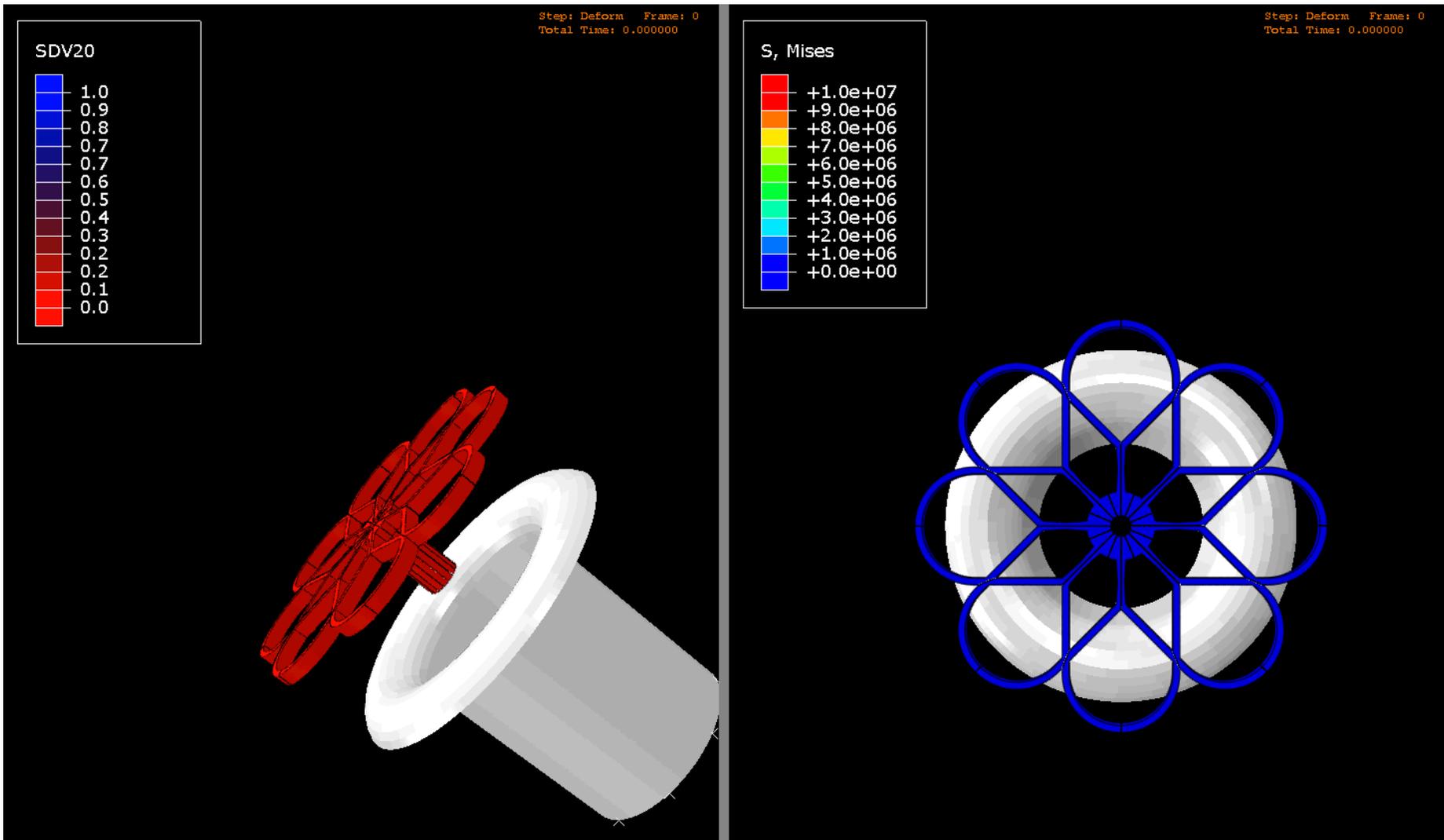
Step: Deform Frame: 0
Total Time: 0.000000



Step: Deform Frame: 0
Total Time: 0.000000

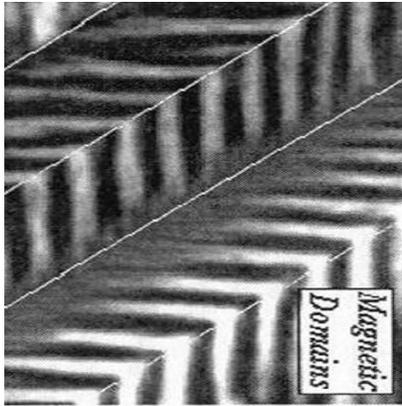


SMP Thrombectomy Device

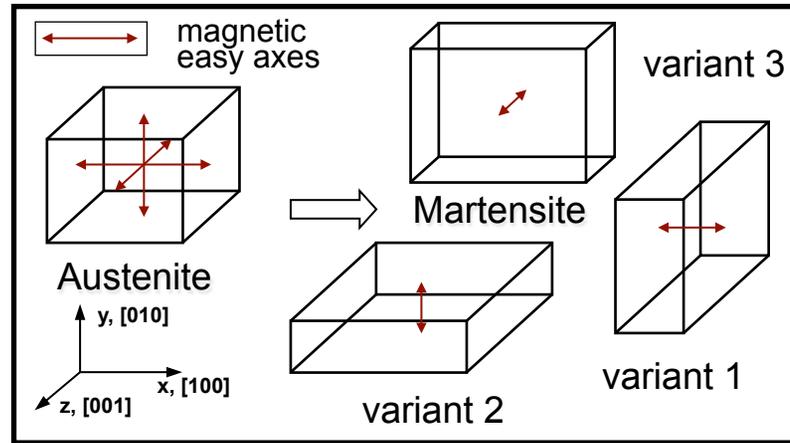


Magnetic Shape Memory Alloys

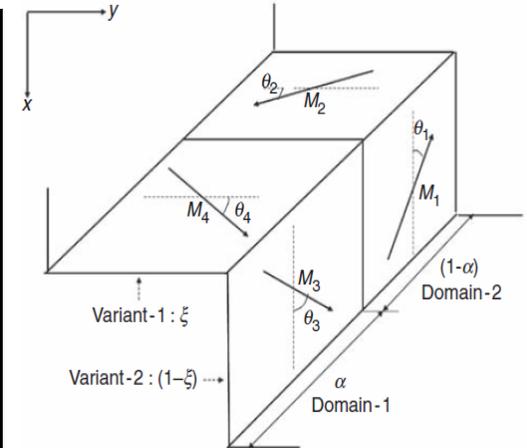
Magnetic Shape Memory Effect



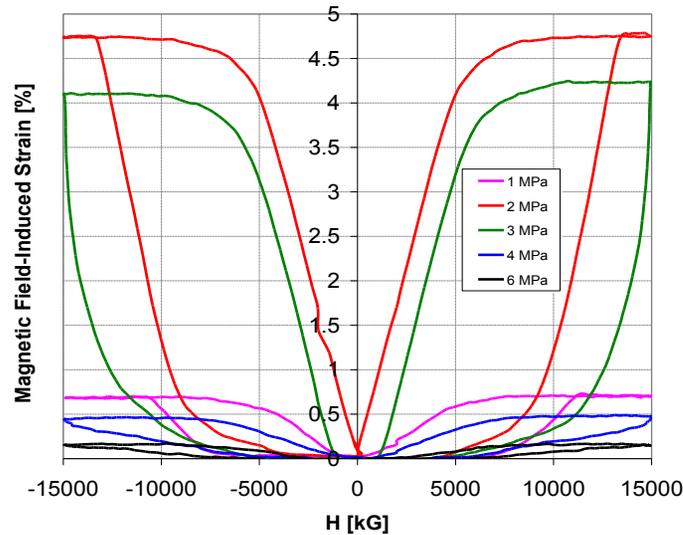
Magnetic Domain Structure



Martensitic Phase Transformation in MSMA



4 possible magnetic domains in tetragonal martensite

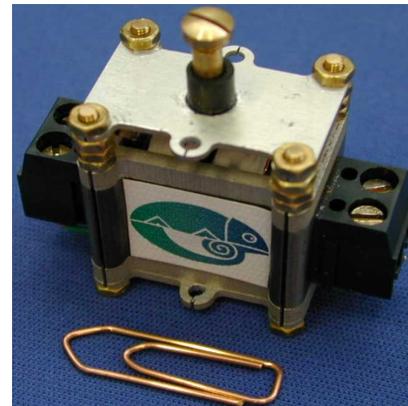
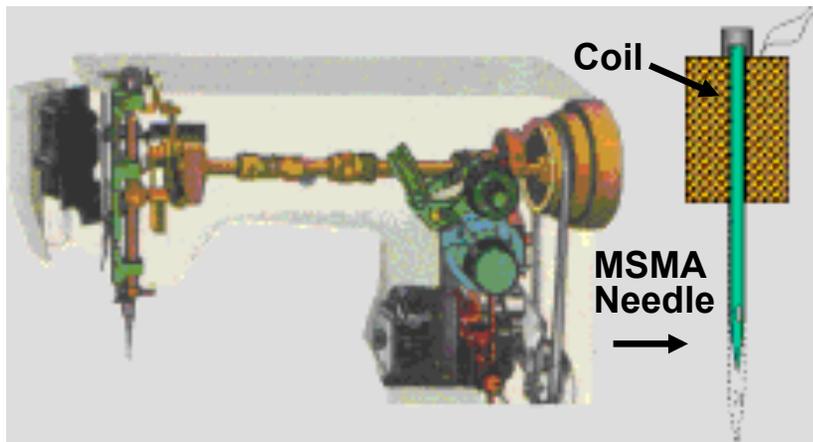
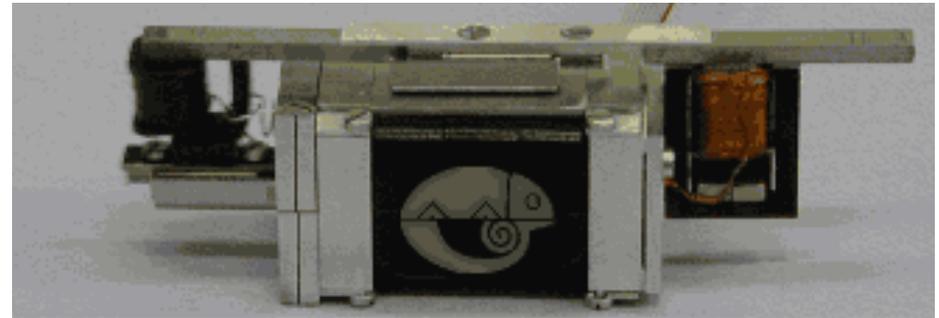


Large magnetic field-induced strains in MSMA single crystals

Applications of MSMA

Design of High Frequency MSMA Actuators

- High mobility of twin boundaries that separate martensitic variants
- High Frequency Actuation



Potential application: Replacement of Motor, Gears and Belts in Sewing Machine with Magnetically Actuated MSMA Needle

Commercially available MSMA Actuators:
(source: <http://www.adaptamat.com>)

Ferroelectric Materials

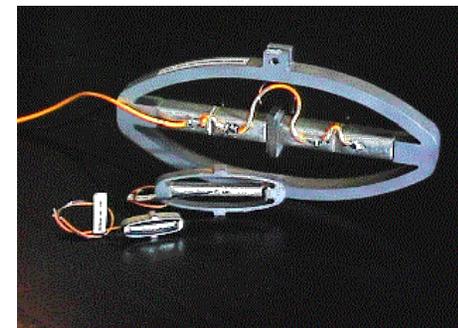
- Ferroelectric materials are defined as those which exhibit, at temperatures below the Curie point, a domain structure and spontaneous polarization which can be oriented by applied electric fields (BaTiO_3 , $\text{Pb}(\text{Zr}, \text{Ti})\text{O}_3$, $\text{Pb}(\text{Mg}, \text{Nb})\text{O}_3$)

Advantages:

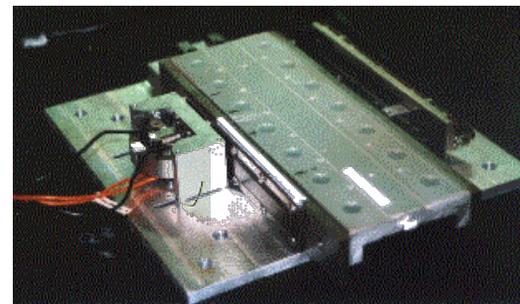
- ◆ Very High Actuation Frequency
- ◆ Direct Electric-Strain Coupling

Disadvantages:

- ◆ Low Energy Output



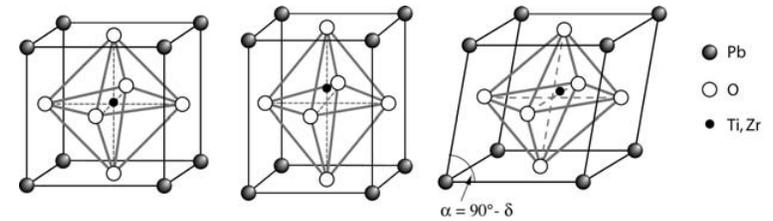
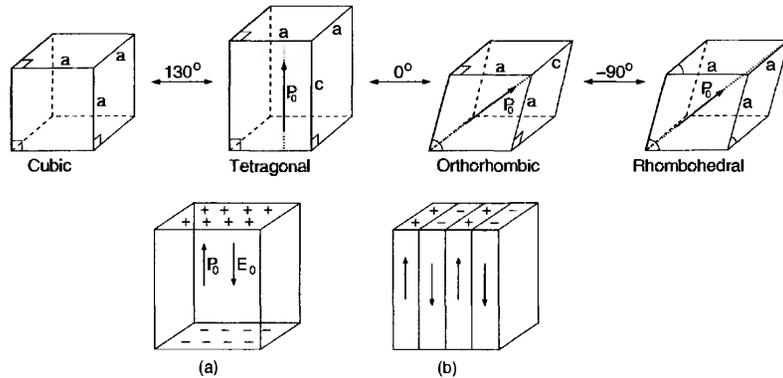
Piezoelectric actuator



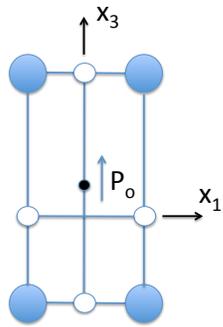
Piezomotor

Direct and Converse Piezoelectric Effects

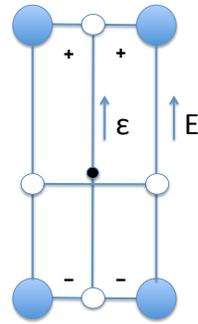
- The *converse piezoelectric effect* constitutes of linear reversible strains generated in ferroelectric materials in response to an applied electrical field
- The *direct piezoelectric effect* designates the opposite phenomenon in which low stress inputs produce changes in the dipole configuration or polarization



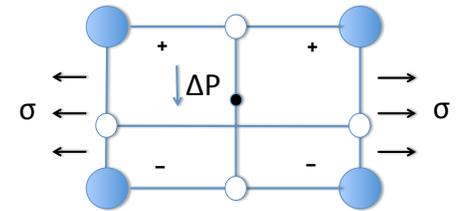
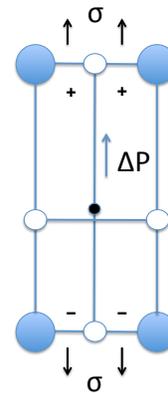
centrosymmetric structure noncentrosymmetric structures



Tetragonal form of PbTiO_3

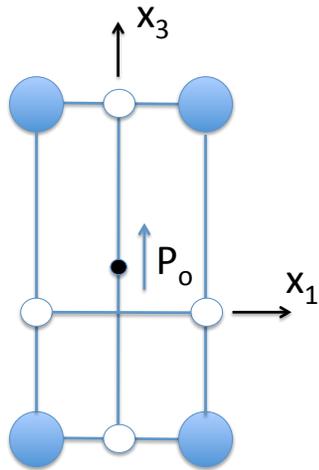


Converse piezoelectric effect
 $\epsilon = d_{33}E$

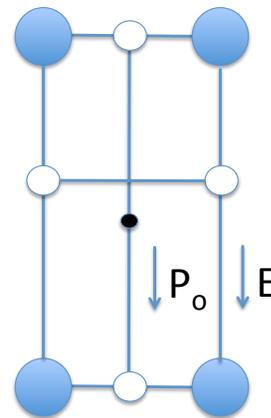


Direct piezoelectric effects
(left) $\Delta P = d_{33}\sigma$ (right) $\Delta P = d_{31}\sigma$ for $\sigma < \sigma_c$

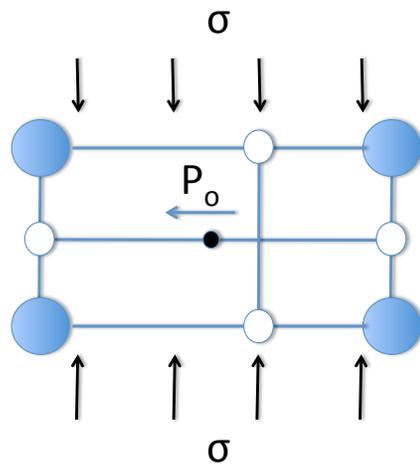
Ferroelectric and Ferroelastic switching



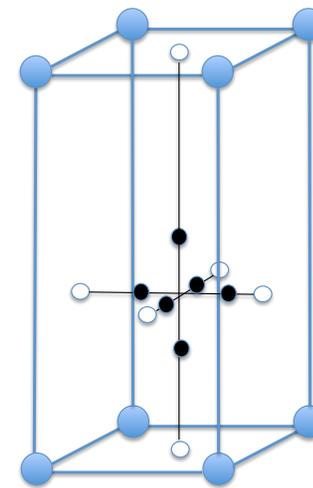
Spontaneous polarization



Ferroelectric 180° polarization switch

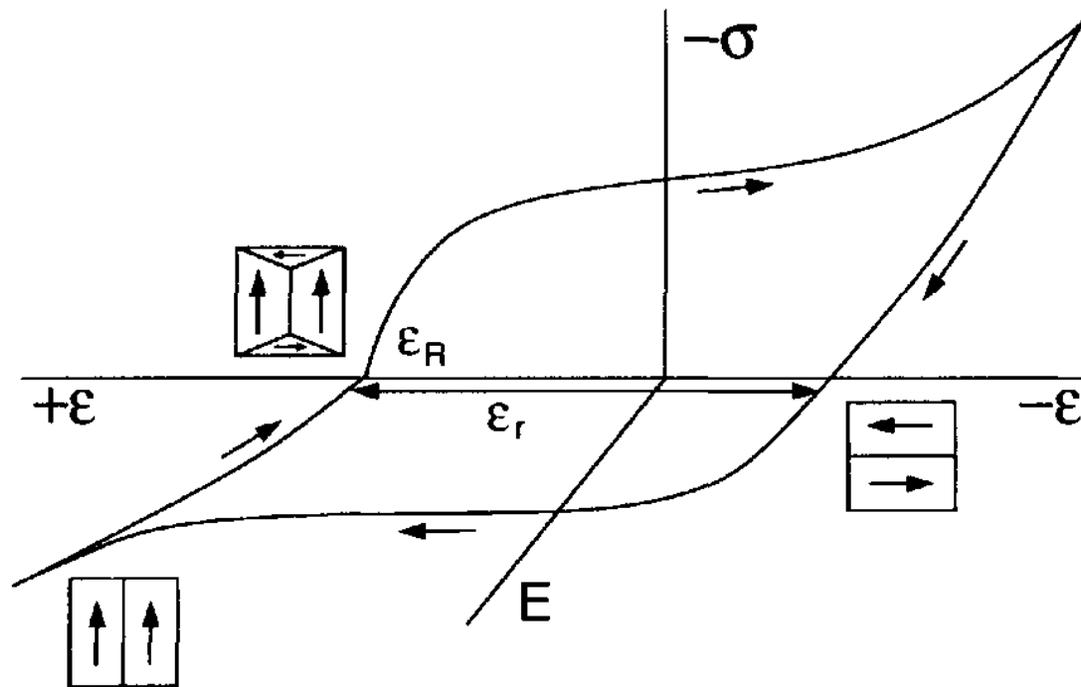


Ferroelastic 90° switch due to compressive stress greater than the coercive stress ($\sigma > \sigma_c$)



Six possible switching mechanisms

Shape Memory Effect



Constitutive Equations for Linear Piezoelectricity

$$\varepsilon_{ij} = s_{ijkl}^E \sigma_{kl} + d_{nij} E_n$$

$$P_n = d_{nij} \sigma_{ij} + \epsilon_{nm}^T E_m$$

σ_{ij} components of the stress tensor

ε_{ij} components of the strain tensor

P_i components of the electric displacement vector

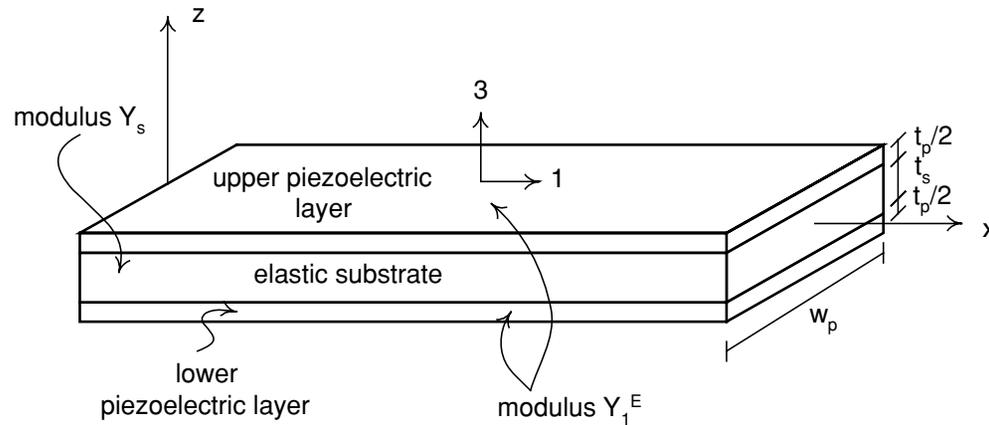
E_i components of the electric field vector

s_{ijkl}^E components of the elastic compliance tensor

d_{nij} piezoelectric strain coefficients

ϵ_{ij}^T components of the permittivity tensor

Extensional Piezoelectric Device



Composite actuator consisting of an elastic substrate and two piezoelectric layers



Electrical connections for a piezoelectric extender actuation. A voltage is applied to the piezoelectric layers aligned with the poling direction of both piezoelectric layers

Extensional Piezoelectric Device (cont.)

The deflection u_1 of a piezoelectric extender of total length L can be expressed as

$$u_1 = \varepsilon_{11} L$$

and the electric field is equal to the applied voltage divided by the piezoelectric layer thickness

$$E_3 = \frac{2v}{t_p}$$

Constitutive relationships for the three layers

$$\varepsilon_{11} = \begin{cases} \frac{1}{Y_1^p} \sigma_{11} + d_{13} E_3, & \frac{t_s}{2} \leq z \leq \frac{1}{2}(t_s + t_p) \\ \frac{1}{Y_s} \sigma_{11}, & -\frac{t_s}{2} \leq z \leq \frac{t_s}{2} \\ \frac{1}{Y_1^p} \sigma_{11} + d_{13} E_3, & \frac{1}{2}(t_s + t_p) \leq z \leq -\frac{t_s}{2} \end{cases}$$

Extensional Piezoelectric Device (cont.)

Integrating over the y and z directions for the respective domains gives

$$\frac{w_p t_p}{2} Y_1^p \varepsilon_{11} = \int_{y,z} \sigma_{11} dydz + \frac{w_p t_p}{2} Y_1^p d_{13} E_3$$

$$w_p t_s Y_s \varepsilon_{11} = \int_{y,z} \sigma_{11} dydz$$

$$\frac{w_p t_p}{2} Y_1^p \varepsilon_{11} = \int_{y,z} \sigma_{11} dydz + \frac{w_p t_p}{2} Y_1^p d_{13} E_3$$

Assuming that the strain in all three regions is the same, by adding one obtains

$$(w_p t_p Y_1^p + w_p t_s Y_s) \varepsilon_{11} = \int_{y,z} \sigma_{11} dydz + w_p t_p Y_1^p d_{13} E_3$$

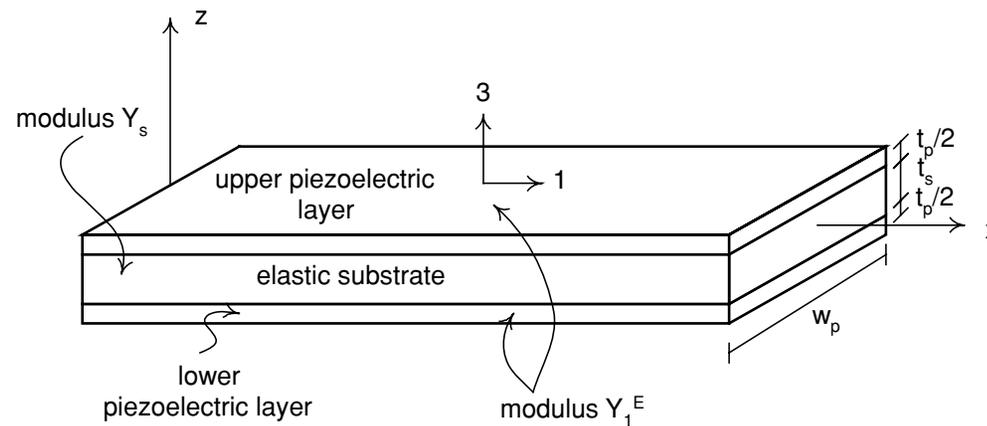
Extensional Piezoelectric Device (cont.)

Thus

$$u_1 = \frac{2}{1 + \Psi_e} \frac{d_{13}Lv}{t_p}$$

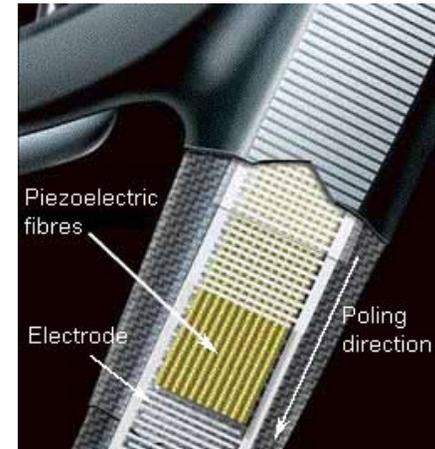
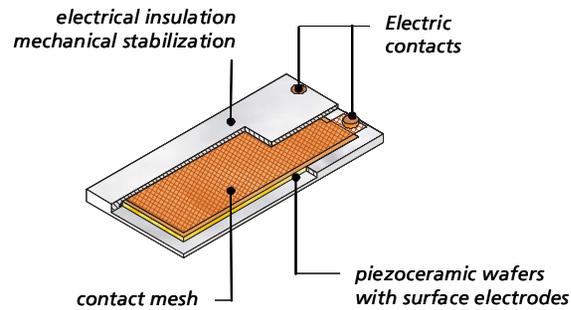
where

$$\Psi_e = \frac{Y_s t_s}{Y_1^p t_p}$$

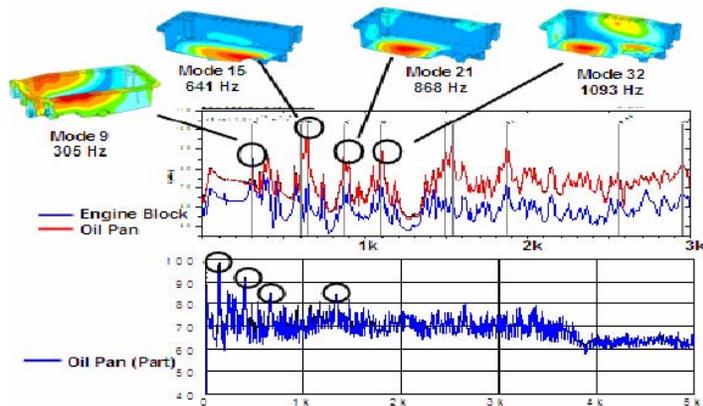


Applications of Ferroelectrics

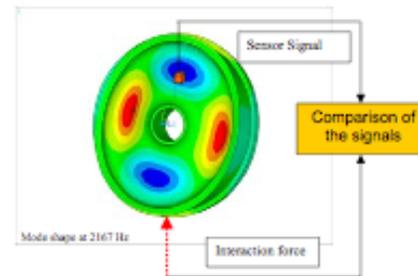
- Medical Ultrasound Imaging
- Transducers
- Hydrophones
- Micro pumps
- Vibration control
- Actuators



High temperature piezoelectric composites. An active damping concept (University of Bath)



Significant noise reduction can be achieved with the use of piezoelectric patches



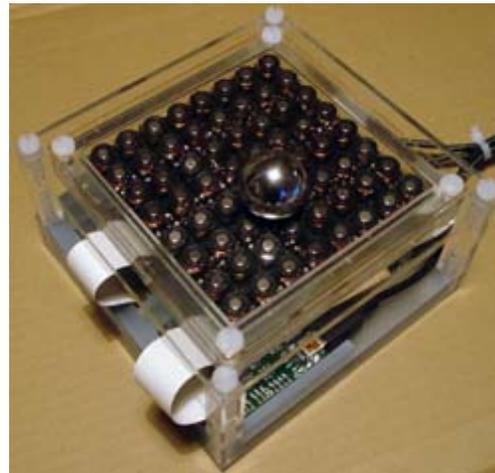
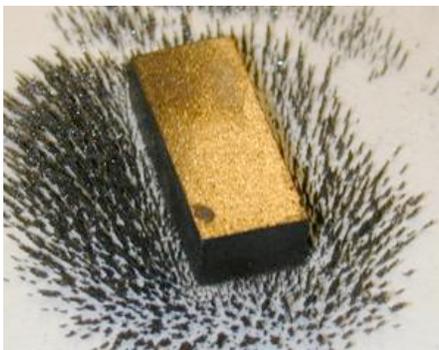
A piezoelectric sensor detects the vibrations of the wheel, leading to an assessment of its wear status

Ferromagnetic Materials

- At temperatures below the Curie point, ferromagnetic materials exhibit a domain structure and spontaneous magnetization which can be oriented by applied magnetic fields (Fe, Ni, Co)

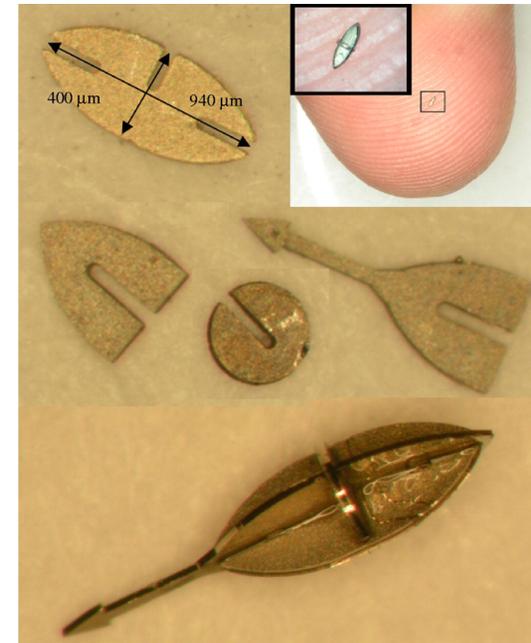
Advantages:

- ◆ Moderate Strains
- ◆ Moderate Force
- ◆ High frequency



Ferromagnetic sensor

<http://research.microsoft.com/en-us/projects/ferromag/>



Source: ETH, Zurich

Miniature ferromagnetic prototype devices can be made to move within fluids by applying an external magnetic field

Polymer Nanocomposites

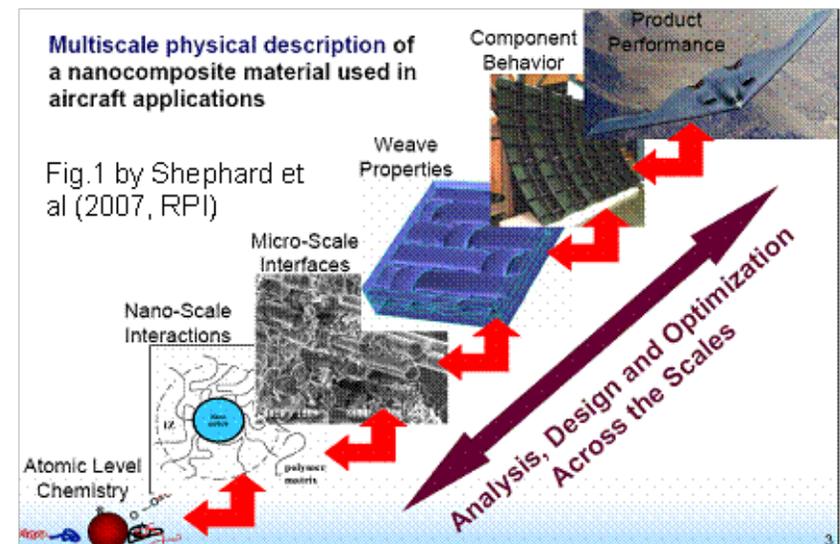
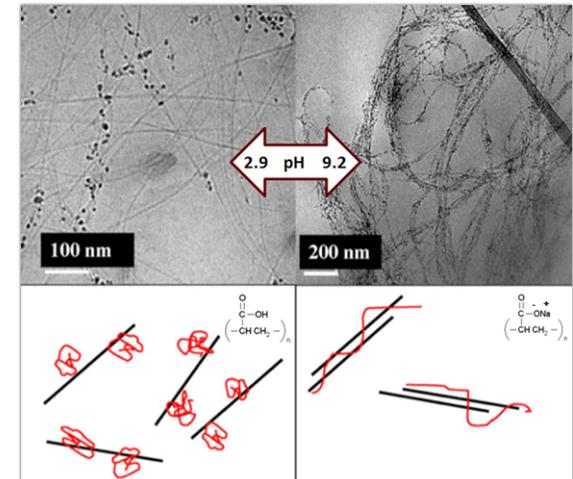
Polymer nanocomposites consist of a polymeric material (e.g., thermoplastics, thermosets, or elastomers) with reinforcement of nano-particles

Most commonly used nano-particles include:

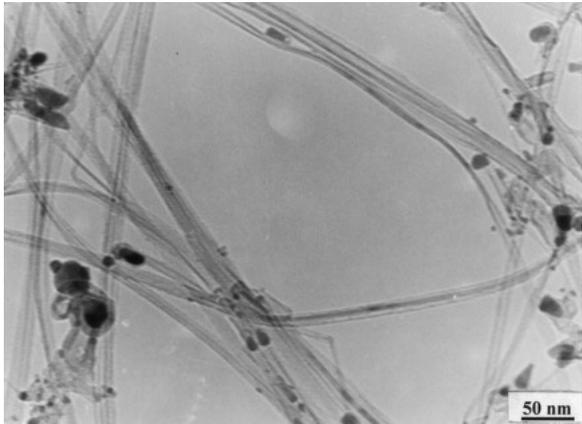
- ◆ Carbon nanofibers (CNFs)
- ◆ Carbon nanotubes [multiwall (MWNTs), small-diameter (SDNTs), and single-wall (SWNTs)]
- ◆ Nanosilica (N-silica)
- ◆ Nanoaluminum oxide (Al₂O₃)
- ◆ Others

Thermosets and thermoplastics used as matrices for making nanocomposites include:

- ◆ Nylons
- ◆ Polyolefin, e.g. polypropylene
- ◆ Polystyrene
- ◆ Ethylene-vinyl acetate (EVA) copolymer
- ◆ Epoxy resins

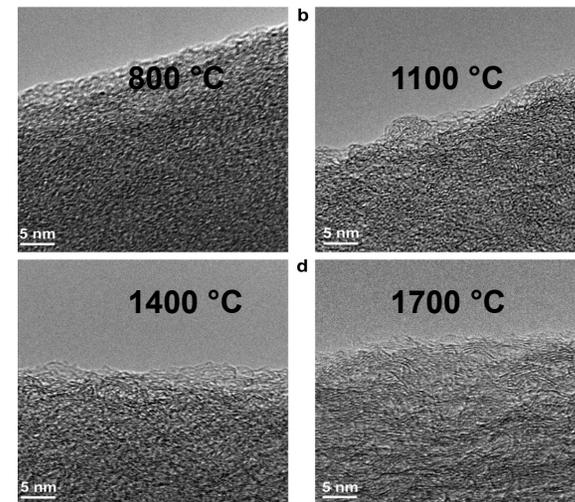
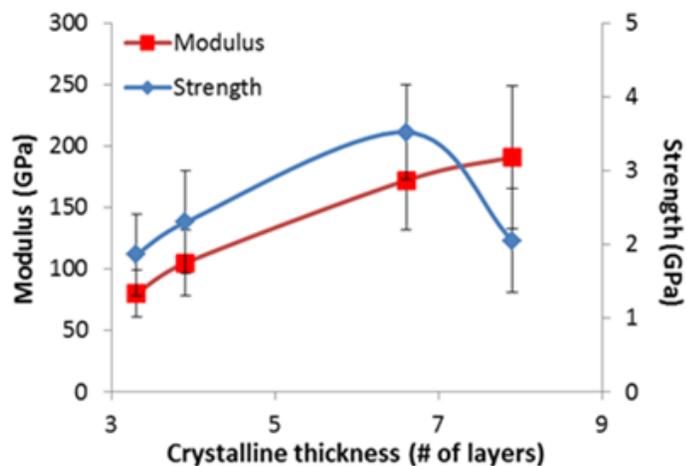


Carbon NanoFibers



TEM image of several CNFs

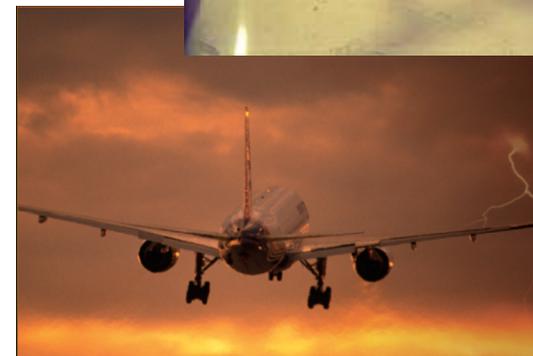
- Due to the remarkable mechanical properties, high thermal stability and electrical properties, CNFs offer opportunities to develop multifunctional materials
- Role of the interphase around the inclusion:
 - Polymer with restricted chain mobility
 - Higher Tg, Stiffness, Strength



Thermal stability of CNFs

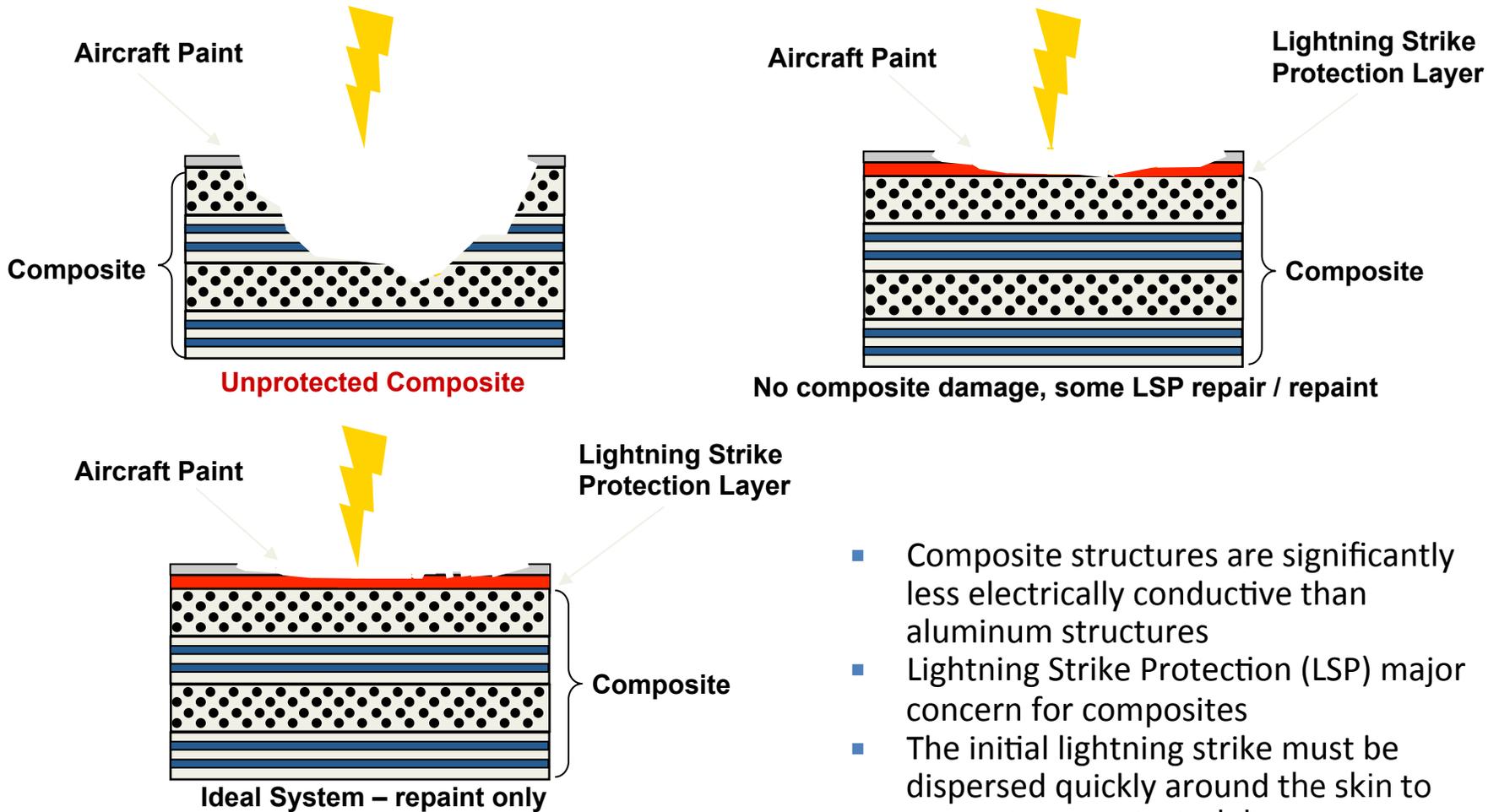
An Application of Polymer Nanocomposites

- Lightning strikes cause:
 - resin melting, vaporization, and ply delamination in composites
 - Increase in affected area
 - Compromise structural integrity of aircraft
 - Difficult to repair
 - damage to onboard electronics without EM shielding
- Current LSP system protects composites from complete failure
 - But large damage still present
- Avoiding weather not always an option



1. <http://abcnews.go.com/Travel/Story?id=3994564&page=1>
2. <http://www.lightningtech.com/d~ta/faq1.html>
3. http://www.boeing.com/commercial/aeromagazine/aero_10/loop.pdf

Motivation



- Composite structures are significantly less electrically conductive than aluminum structures
- Lightning Strike Protection (LSP) major concern for composites
- The initial lightning strike must be dispersed quickly around the skin to prevent concentrated damage

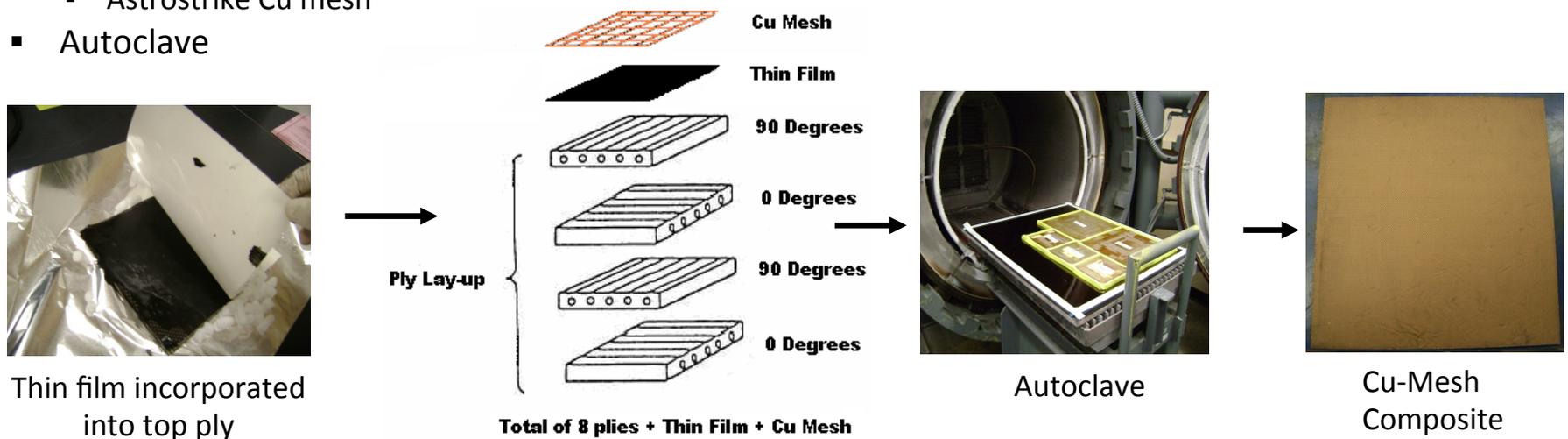
Fabrication

- Carbon nanotube thin film fabrication



- Incorporate thin films into composite laminate structure

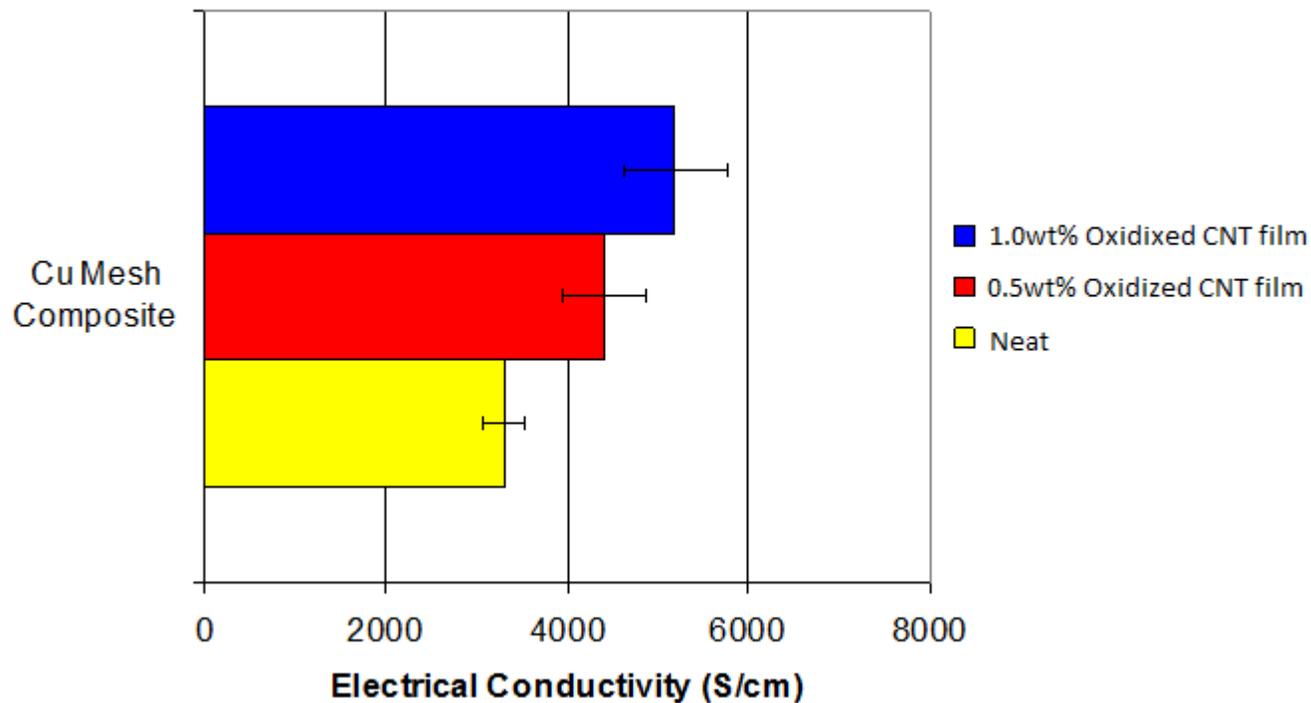
- Embodiment CNT loaded resin thin film on top carbon fiber ply
- Lay-up rest of carbon fiber and Cu mesh
 - T650-135 carbon fiber plies
 - Astrostrike Cu mesh
- Autoclave



Electrical Conductivity

- Composite Electrical Conductivity

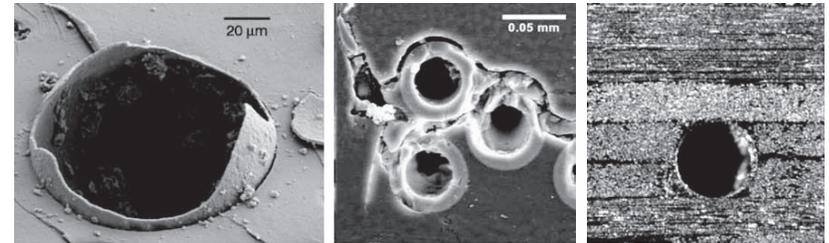
Electrical Conductivity of Composites



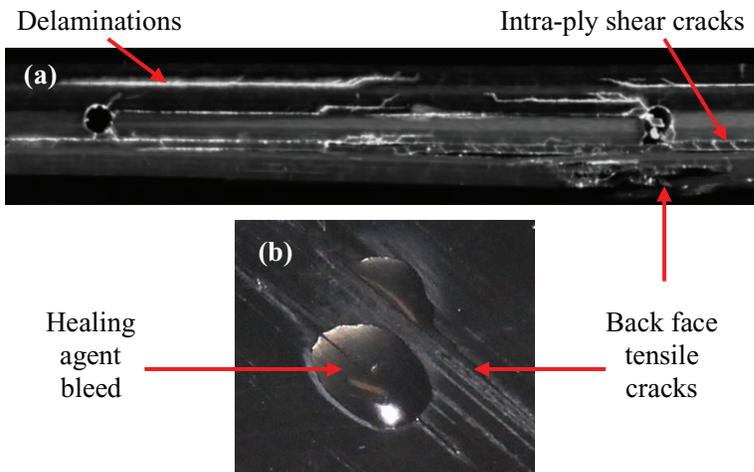
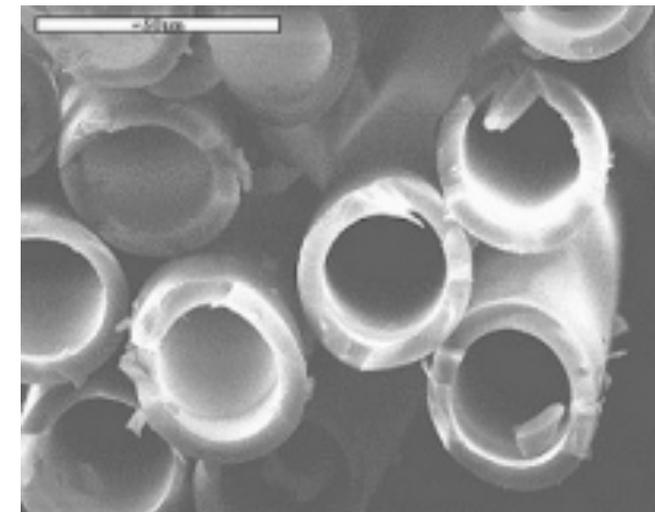
- Increase of about 1000 S/cm from control to 0.5 wt% and from 0.5 to 1.0 wt%

Self-Healing Composites

- Self healing can be described as mechanical, thermal or chemically induced damage that is repaired by materials already contained within the structure
- The release of repair agent from embedded storage reservoirs mimics the bleeding mechanism in biological organisms. Once cured, the healing resin provides crack arrest and recovery of mechanical integrity
- Experiments have shown as much 75% recovery of the original strength



storage reservoirs



Self-Healing Fibre Reinforced Composites via a Bioinspired Vasculature

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Christopher J. Norris, Gregory J. Meadway, Michael J. O'Sullivan, Ian P. Bond, and Richard S. Trask