SAND2008-4731P

Physical & Engineering Sciences Center
Atoms to Continuum

Technology Symposium Series

Active Polymer Composites for Detecting Abnormal Thermal and Optical Environments

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National Nuclear Security Administration

Sandia National Laboratories

Presentation Overview

- Our goal: self-powered sensors & actuators
- Who's on our team
- Our research:
  - Synthesis of Light Activated Polymers
  - Characterization of Heat Activated Polymers
  - Development of Predictive Material Models
  - Design of Active Polymer Devices
- Where are we headed

Advanced Sensors & Actuators

We need smart structures and devices to:

- detect specific temperature or light exposures
- actuate responses through large deformation
- generate an electrical signal to verify actuation
- initiate further action

Polymer Composites, a Solution?

- **Idea for LDRD: Develop new flexible active composites by combining shape memory polymers (SMP) and piezoelectric materials.**

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Has This Been Done Before?

- **While some have used piezoelectric materials to activate a response in electro-active SMPs, no one has used SMPs to stimulate piezoelectrics.**
- **Our focus is to investigate this possibility for constructing self-powered devices.**

Our Project Team

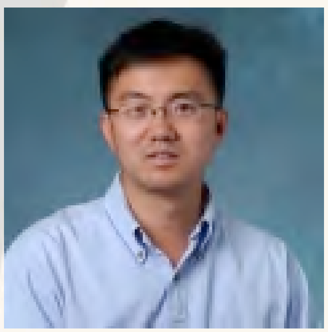
L.A. Domeier and A. Nissen (8778): Formulation, testing and application of polymers

J.R. McElhanon (1821), G. O'Bryan (8778): Design of light-responsive SMPs

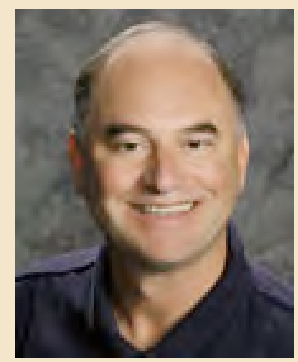
A. Mota (8776): Finite element modeling and analysis of piezoelectric materials

Our Project Team

T.D. Nguyen (Johns Hopkins University): FY07 PI, Finite element modeling of polymers



H.J. Qi (University of Colorado at Boulder): Development of material models for polymers and testing.

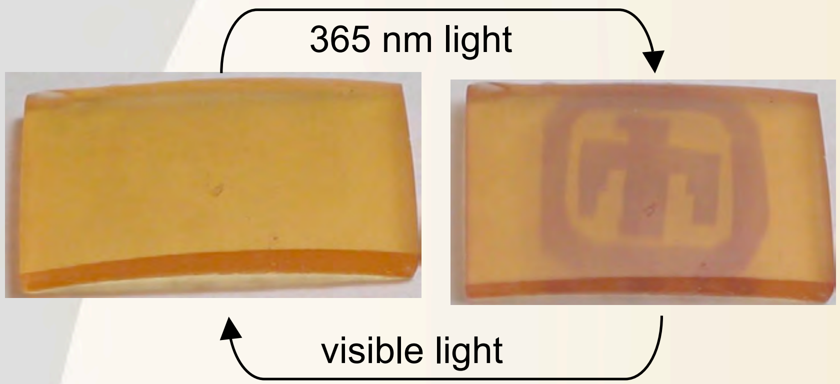


E.P. Chen, M.L. Chiesa (8776): PM

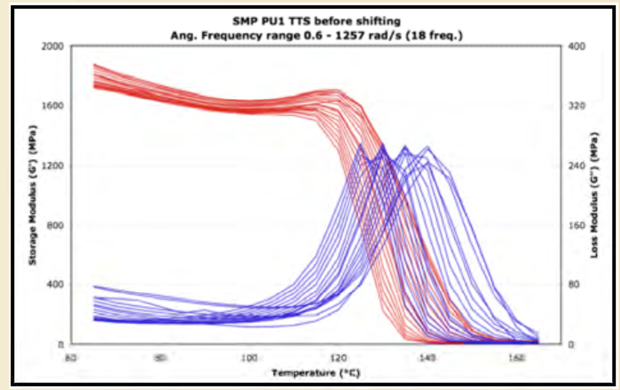
J.A. Zimmerman (8776): PI

Project Work Areas

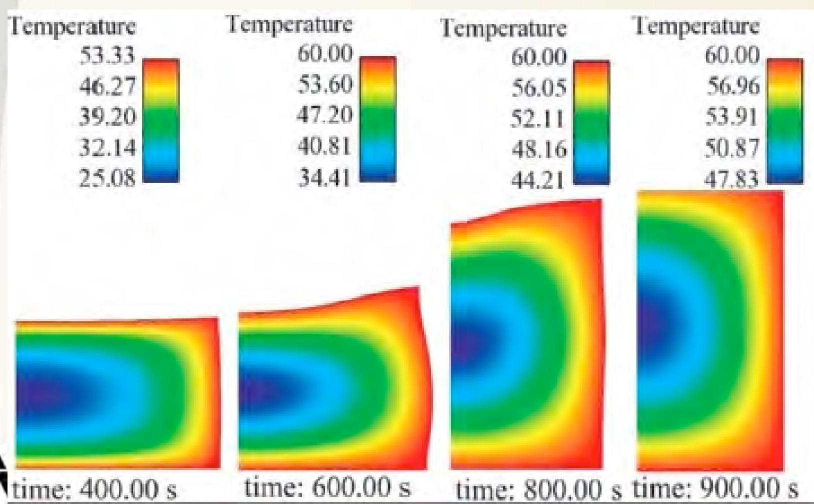
Synthesis of Light Activated SMPs



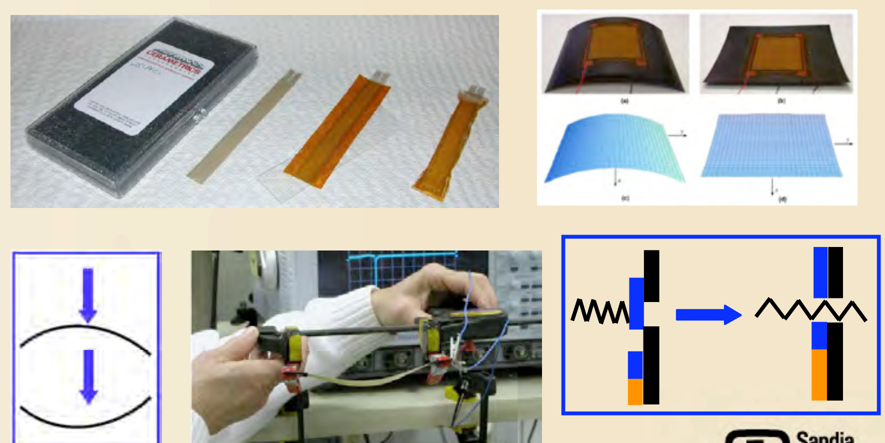
Characterization of Heat Activated SMPs



Development of Material Models



Design of Active Polymer Devices



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(Visible) Light Activated SMPs

Technical Challenge:

Create light activated SMPs that respond to ambient light (500-700 nm).

General Desired Characteristics:

- Change shape when exposed to specific light wavelengths.
- Fast response time, low stiffness, weak stress recovery.
- Possible 2-way shape change

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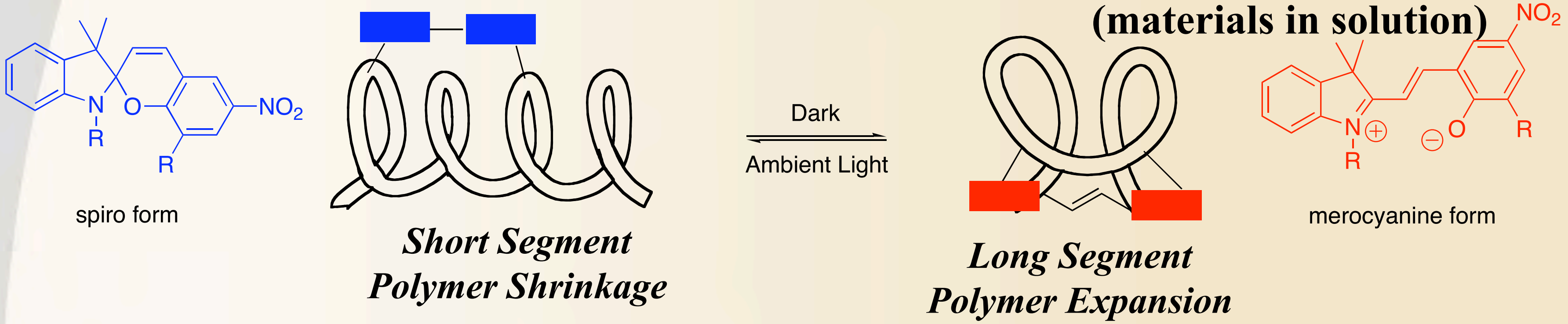
Molecular Mechanism

Microstructure: permanent segments connected by switching cross-links.

Switching mechanism: reversible bond cleavage / formation, conformation change.

Fujimoto *et al.*, 2005.
(materials in solution)



- Dimensional changes of crosslinker can yield large macromolecular shape changes.
- Response depends on crosslink density, monomer proportions, mobility of connecting segments.

Light Activated Methacrylate Elastomer SMPs

Strategies:

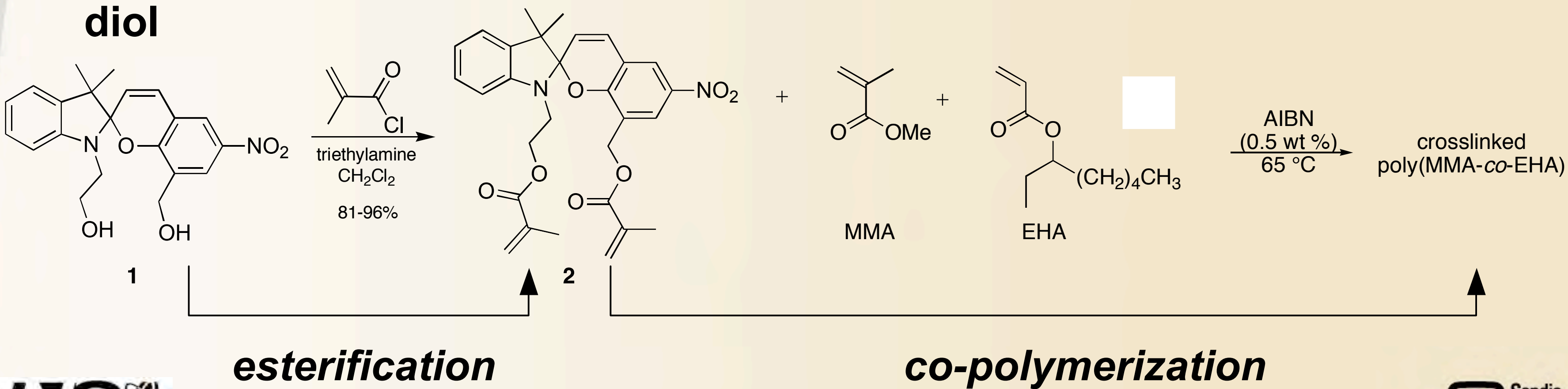
- Develop transparent elastomer with di-substituted spyropyran (SP) crosslinkers.
- Exploit the photo-reversible ring opening mechanism of spiropyran molecules.
- Optimize chain mobility, cross-link MW to enhance macromolecular shape change.

Formulation Strategies

Strategies:

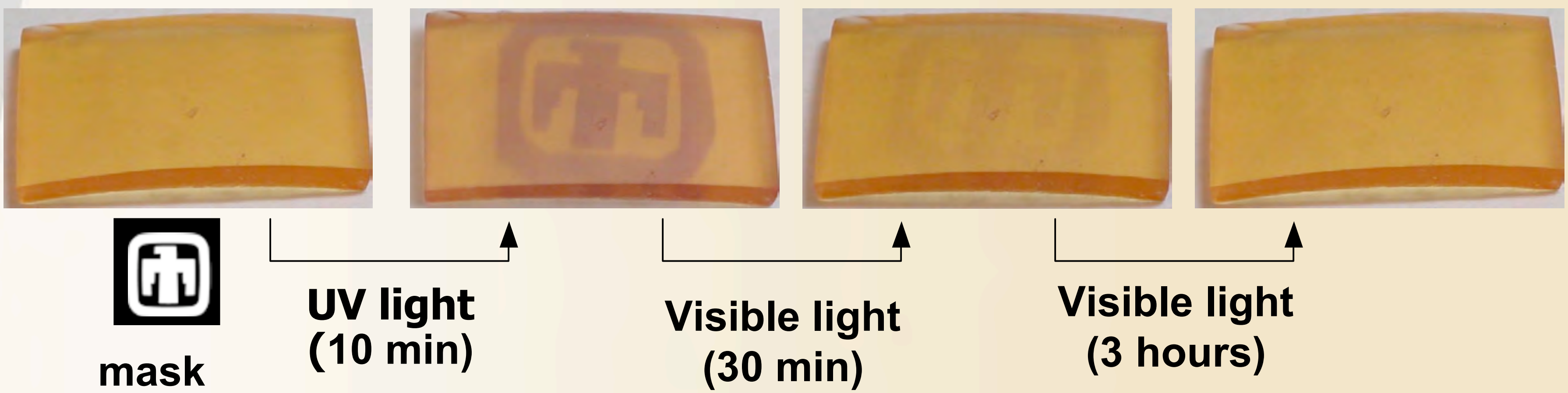
- **Methacrylates containing spiropyran crosslinkers are formulated into photoactive polymer films.**
- **Polymer properties (Tg, swelling, etc.) are tuned by varying the monomer and crosslinker ratios.**

SP-containing diol **SP-containing dimethacrylate crosslinker**



Synthesized Light Activated SMPs

SP units change from colorless to purple upon exposure to UV light and reverse this effect upon exposure to visible light. No significant dimensional changes seen, however.



More To Do: Get a Deformation

Further testing/formulating to optimize potential shape memory effects:

- crosslinking (*inter-chain* responses)
- chain stiffening (*intra-chain* responses)

Alternative polymeric systems:

- Mixtures of polycaprolactone and polyurethane to produce a two-switch material, I.e. stress is induced thermally but alleviated by irradiation.
- Urethanes with chain stiffening compositions

Heat Activated SMPs

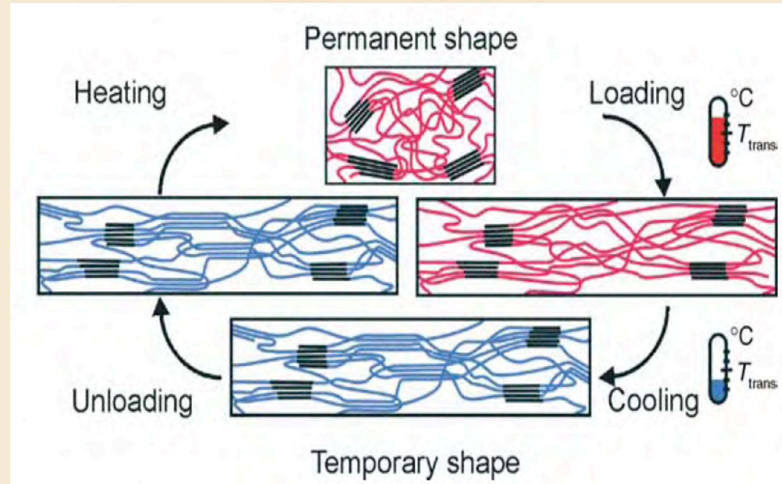
General Characteristics:

Most polymers, to some extent, are SMPs.

Lendlein, 2005

Molecular Mechanisms

Permanent shape determined during processing: temporary, stressed shape "programmed" by heat-stress-cool cycle above Tg.



- **Switching mechanism: rubber-glass or crystalline-melt transition.**
- **Response depends on crosslink density and spacing, chain stiffness, chain mobility and thermal conductivity.**

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Technical Challenges and Directions

- Identify high-performance SMPs.
- Characterize their properties to provide data that can be used in material models.
- Improve properties:
  - sharpen temperature sensitivity
  - improve response times
  - stiffen stress recovery
  - maintain or improve toughness

But: Polymers are inherently limited by their viscoelastic nature.

Lab Work on Heat Activated SMPs

- Some reported systems (LLNL) have shown very poor processability.

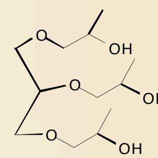
- Commercial systems examined have shown notable brittleness and slow response times.

- Screening experiments had shown a Sandia urethane to have SMP properties, toughness and processability as good or better than any other systems.

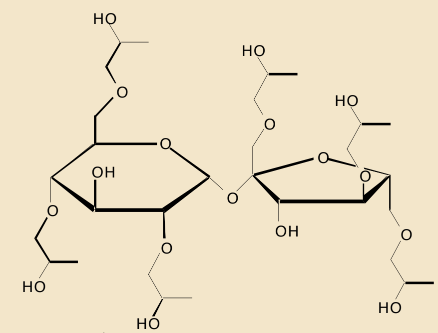
SMPU (Shape Memory Polymer Urethane) Variants

The initial SMPU formulation (SMPU-0) was non-stoichiometric (closer to foam formulation).

Adjustments to the OH/NCO stoichiometry (SMPU-1) lowered the Tg and also, noted much later, reduced the toughness.



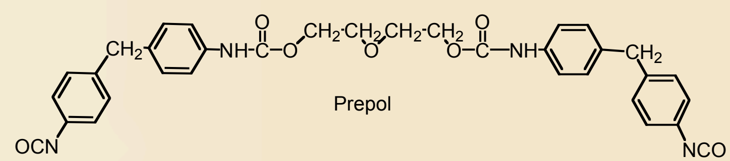
60% Glycerol•3 Propyleneoxide
MW=266
fcn=3



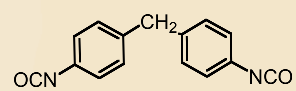
40% Sucrose•6 Propyleneoxide
MW=690
fcn=8

Hydroxyl (OH) containing components

V490
MW=460
fcn=4.3



Prepol



MDI

Isocyanate (NCO) containing components

	I-2181
Prepol	32%
MDI	68%

Properties of SMPUs

Reducing both Tg and toughness is unusual and highlights the particular toughness of the foam and related formulations.

TMA and DMA characterizations were carried out on the "correct", lower Tg SMPU-1. Some will be repeated with SMPU-0.

Ingredient	SMPU-0 (original)	SMPU-1 (adjusted)
Voranol 490 polyether polyol	72.0	72.0
DABCO-33LV catalyst	0.17	0.15
Isonate 181 diisocyanate	134.05	108.48

Characterization of SMP Behavior

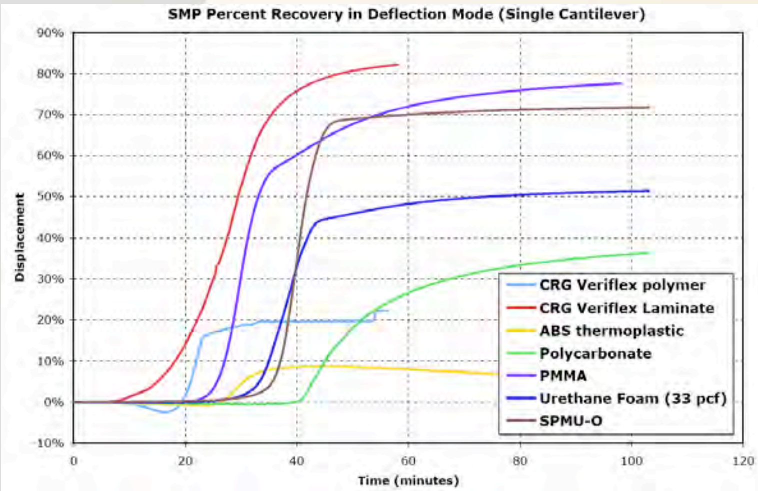
Technical Approach

- Properties measured in TMA and DMA experiments.
- SMP recovery behavior of samples measured in bending, compression and tension.
- SMPUs, commercial SMPs, heat shrink sheet and films were all characterized.

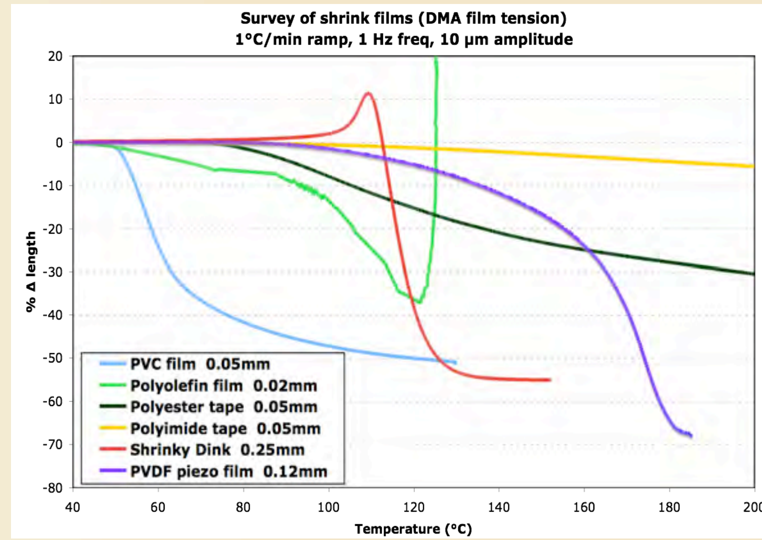
Dynamic Mechanical Analysis (DMA)

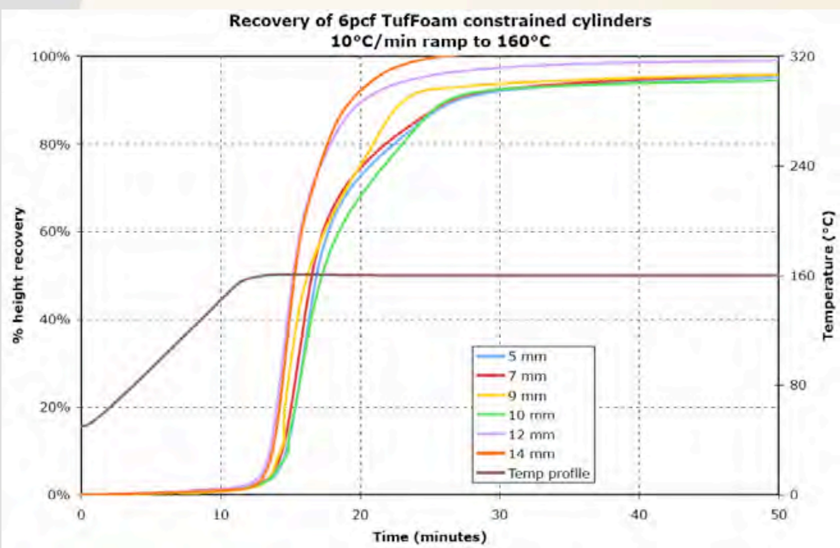
Thermal Mechanical Analysis (TMA) expansion fixture

Evaluating the Best SMPs



SMPU-0 shows excellent cantilever recovery response





Compressed foam cylinders all showed good expansion recoveries with little diameter dependence.

Sheet/film/tape tensile recovery rates were modest.

“Shrinky Dink”

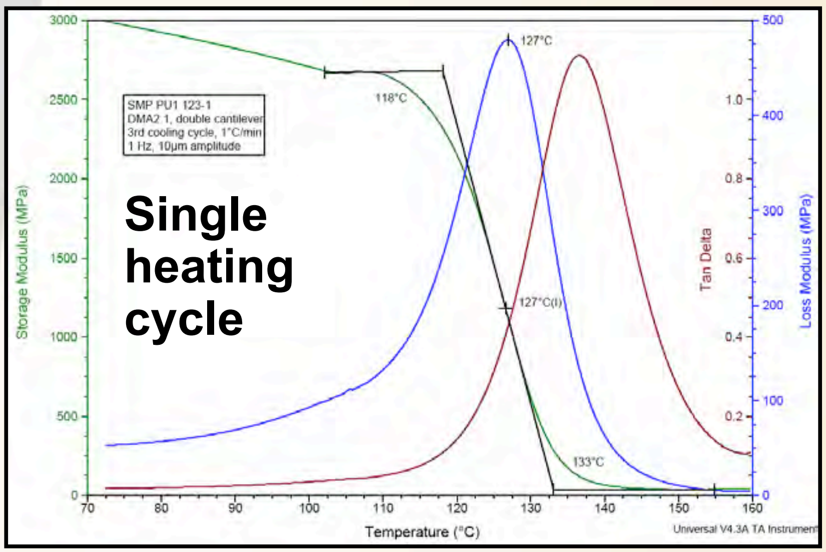
(biaxially oriented polystyrene)

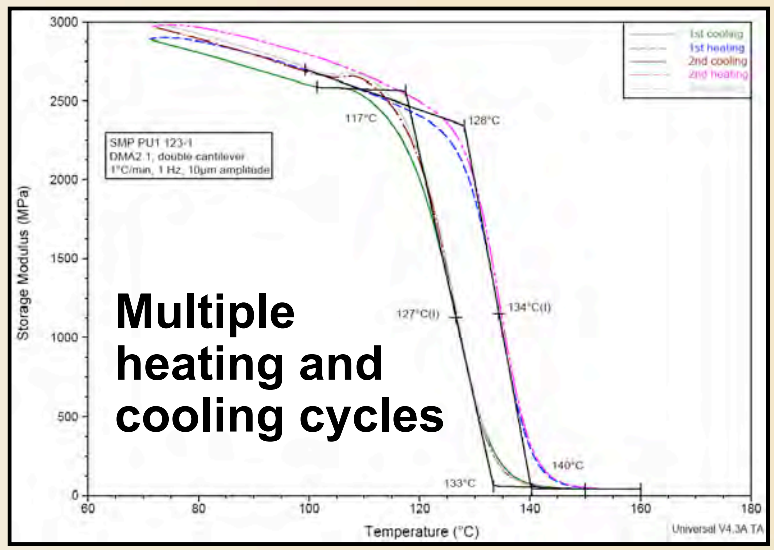
was fastest.

SMPU-1 DMA/TMA Characterization

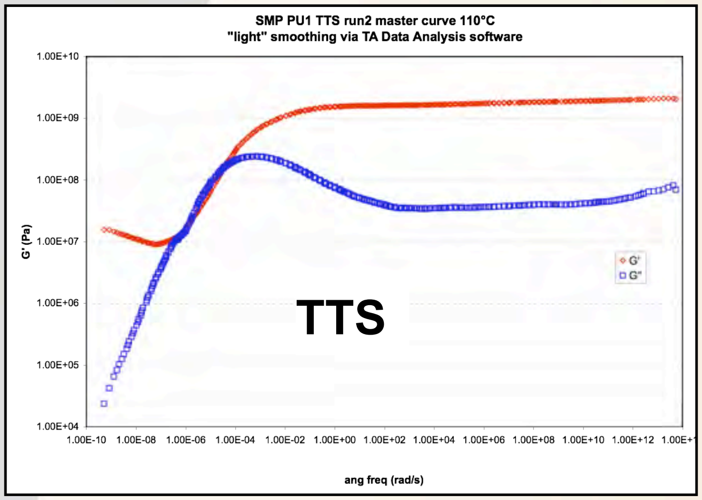
Includes:

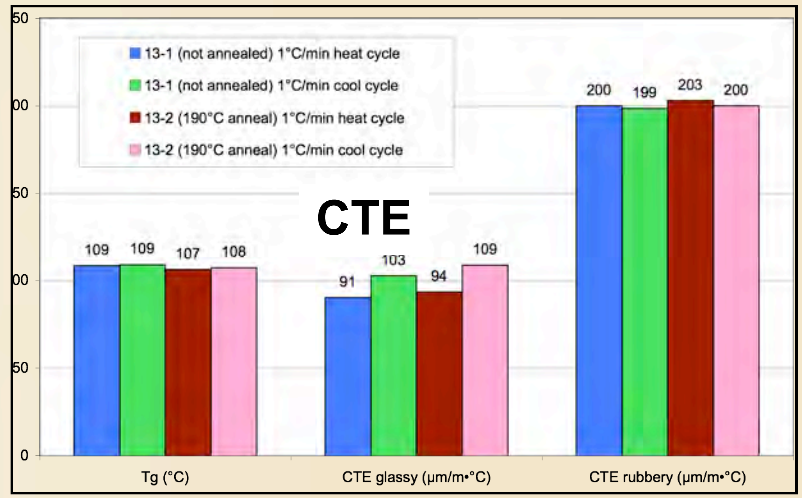
- Tg (heating/cooling, multiple cycles)
- CTE (heating/cooling)
- TTS (Time-Temperature Superposition)
- Compression Creep

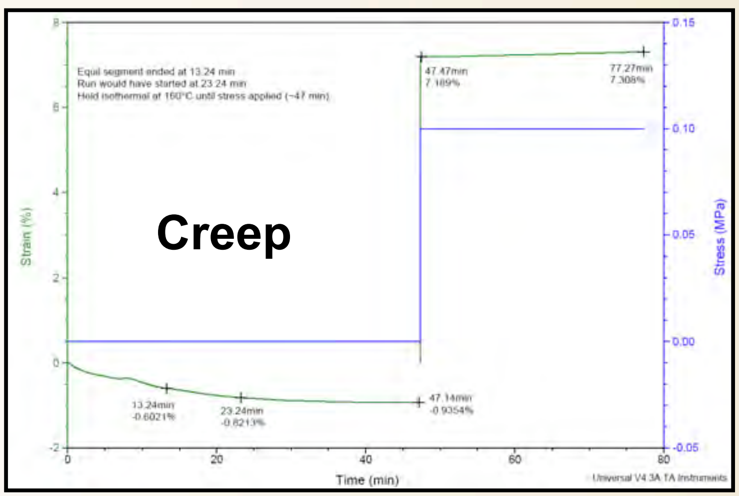


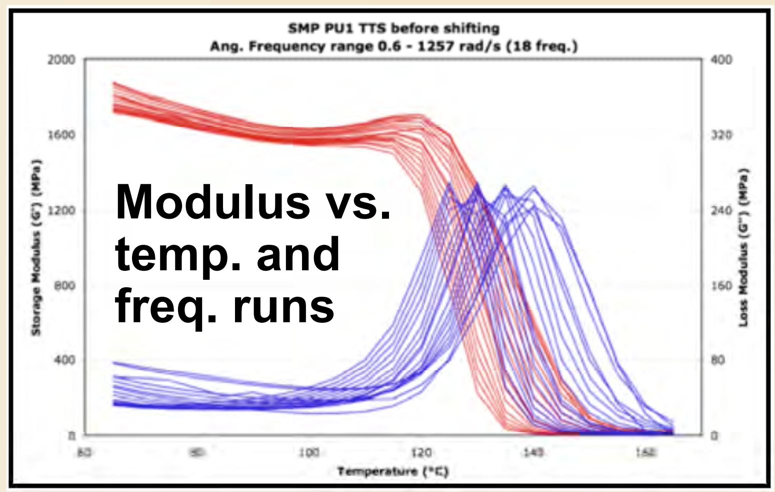


Measurements Required Iteration









Development of SMP Material Model

Technical Challenges:

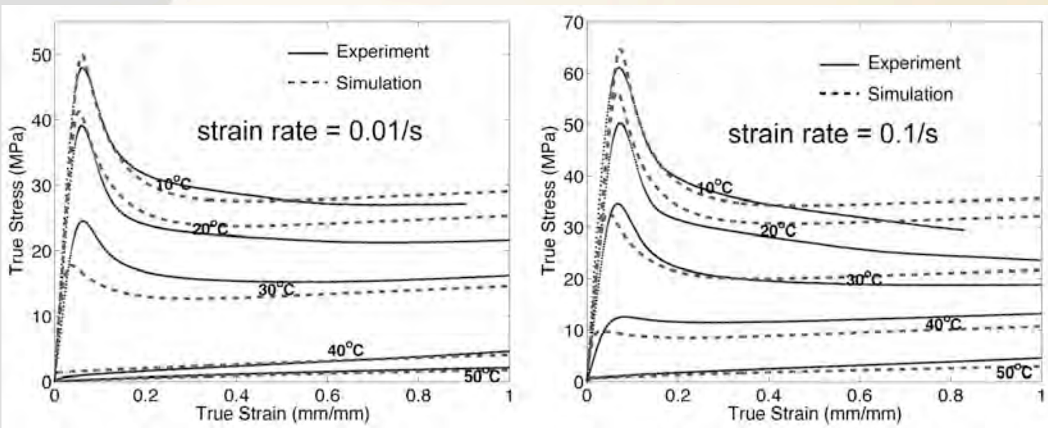
- Develop a model to predict the thermomechanical behavior of SMPs.
- Implement this model and a model for the large deformation of piezoelectric materials into a common FEA framework (code).

Technical Approach:

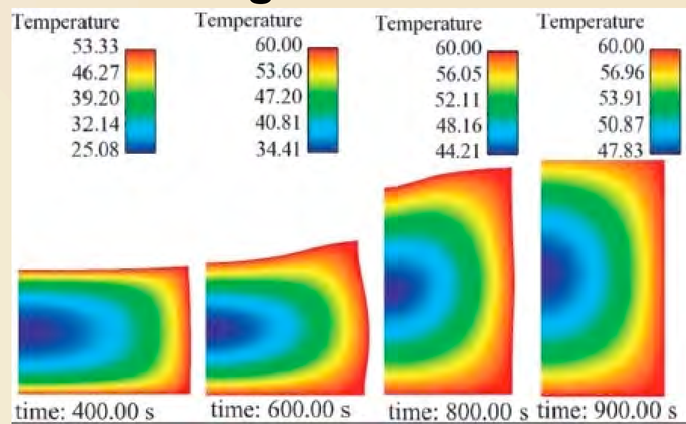
- Incorporate non-equilibrium kinetics of glass transition, deformation recovery and stress relaxation.
- Include dependency of deformation on heating/cooling rates.

SMP Model Shows Realistic Response

Stress-strain response for isothermal, uniaxial compression



Simulation showing non-uniform heating of an SMP device



Publications

Qi, Nguyen *et al*. *Journal of the Mechanics and Physics of Solids*, 2008.
Nguyen, Qi, *et al*. *JMPS*, 2008

More to Do

- **Parameter fitting and validation for SMPU-0.**
- **Use of SMP and PZT models to guide trigger device design.**

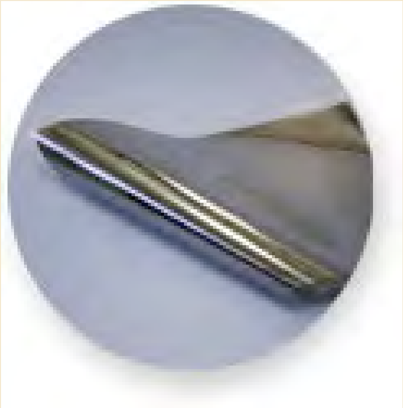
Commercial Piezoelectric Materials

PVDF Piezo Film and PZT Ceramic Fibers

- Devices can be free of external power sources
- Converts mechanical energy to electrical energy
- Can power independent electronic systems
- Flexible, Conformable, Lightweight

PVDF Piezo Film: MSI Sensors

- Available as very thin and flexible sheets (28 micron)
- Voltage Output > 830 V



Piezo PVDF Film (metal on both sides)

Commercial Piezoelectric Materials

PZT Fibers: Advanced Cerametrics

- Ceramic lead zirconium titanite
- Fiber diameters from 5 -250 µm
- Voltage Output - Up to 700 V

Piezo Fibers (embedded in various materials and shapes)

But...the input rate required for any of these is much faster (< second, vibratory) than even the fastest SMP can provide.

Piezoelectric Material Model

Technical Approach

- Reformulate a constitutive model for piezoelectric materials in the material (undeformed) configuration.

$$\mathbf{d}(\boldsymbol{x},t) = \varepsilon \mathbf{e}(\boldsymbol{x},t) \quad \longrightarrow \quad \boldsymbol{D} = J\boldsymbol{F}^{-1}\boldsymbol{d}, \quad \boldsymbol{E} = \boldsymbol{F}^T\boldsymbol{e}$$

compatibility

$$\boldsymbol{D}(\boldsymbol{X},t) = -\text{Curl}\ \psi(\boldsymbol{X},t)$$

$$\boldsymbol{F} = \text{Grad}\ \boldsymbol{\varphi}$$

equilibrium

$$\text{Div}\ \boldsymbol{D}(\boldsymbol{X},t) = 0$$

$$\text{Div}\ \boldsymbol{P} + \rho_0\boldsymbol{B} = \rho_0\ddot{\boldsymbol{\varphi}}$$

constitutive model

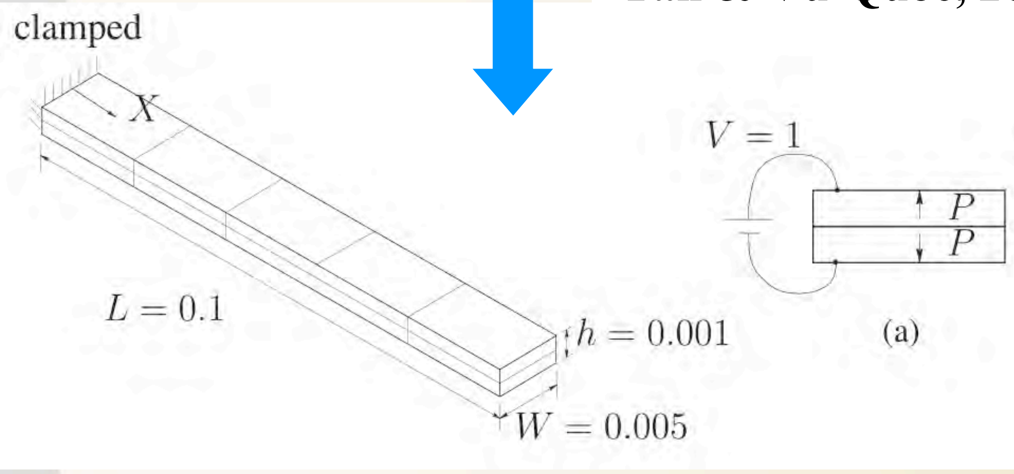
$$A(\boldsymbol{F},\boldsymbol{D},\boldsymbol{Z},T) = W^m(\boldsymbol{F},\boldsymbol{Z}^M,T) + W^r(\boldsymbol{F},\boldsymbol{D},\boldsymbol{Z}^E,T) + W^z(\boldsymbol{F},\boldsymbol{D},\boldsymbol{Z},T)$$

$$\boldsymbol{P} = \frac{\partial A}{\partial \boldsymbol{F}} \qquad \boldsymbol{E} = \frac{\partial A}{\partial \boldsymbol{D}}$$

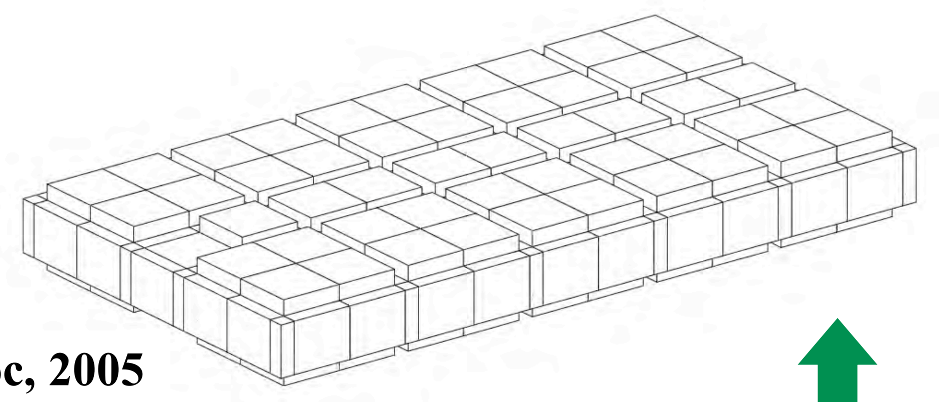
Verification of PZT Model

- **Complete implementation of model in FEA code.**
- **Perform verification example simulations:**

Piezoelectric bimorph beam (two layers of PVDF bonded and polarized in anti-parallel directions



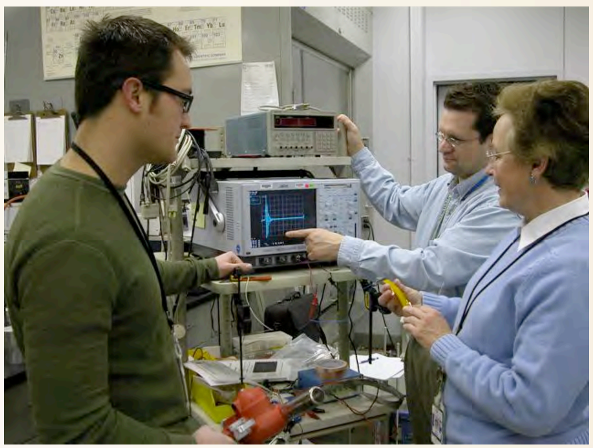
Tan & Vu-Quoc, 2005



Cantilever plate with piezoelectric actuators: Apply differing voltage to plate and actuators alters deflection of plate.

SMP-Piezoelectric Laminate Testing

Simple stitched or taped laminates were assembled using "Shrinky Dink" sheet and Advanced Cerametrics piezo strips. "Control" piezoelectric testing done by hand manipulation.



SMPU-1 was cast around a piezoelectric strip. When heated and deformed over a cylinder, it cracked upon cooling.

PVDF Also Exhibits SMP Behavior

- PVDF is stretched during the poling process and exhibits SMP behavior.

- No electrical response was seen from any of the laminates or the PVDF film during the SMP response.

- These results demonstrate the very different time constants of viscoelastic polymers and piezoelectric materials.

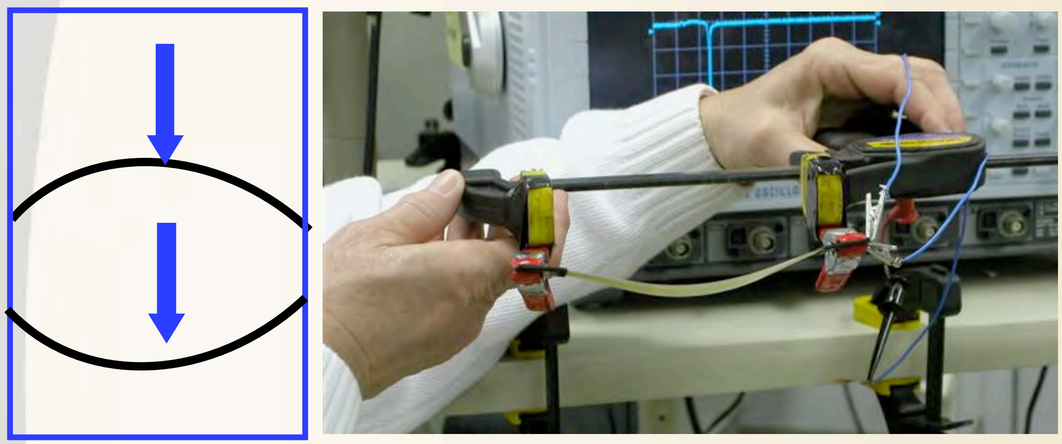
Direct stimulation of a piezoelectric by an SMP is not feasible.

PVDF film before and after shrinkage.

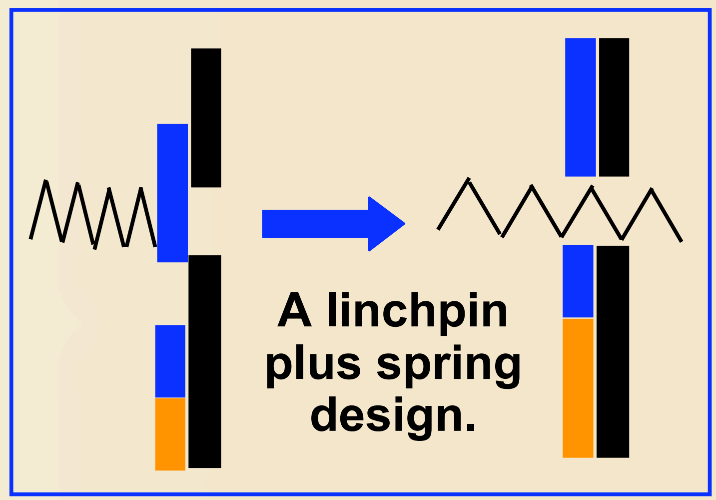
Development of Active Polymer Devices

- Trigger mechanisms are needed to enable the visco-elastic response of a shape memory polymer to provide the vibratory stimuli needed by a piezoelectric material.

- Both bistable switches and linch-pin type designs are obvious candidates.



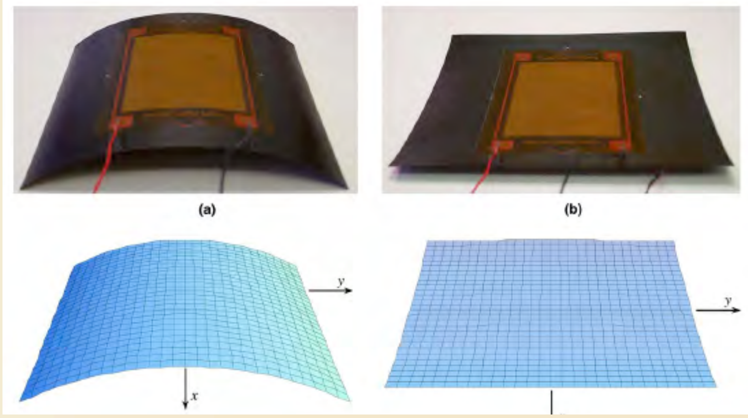
A bistable piezoelectric strip switch was tested “by hand” and gave a 4 V signal.



A linchpin plus spring design.

Interactions with Industry for APDs

- CTD has also developed heat-actuated SMP deployable solar collectors and antenna reflectors.
- Microbuckling of the fiber reinforcement is key to the recoverable response.



CTD laminates “flipped” by a piezoelectric.

No one has used SMPs (foams, sheets or composites) to stimulate piezoelectrics, but design possibility exists.

Both heat and light sensitive SMPs capable of operating a mechanical switch are being pursued.

SMP "Realities" and the Path Forward

- The different response rates of SMPs and piezoelectric materials preclude direct SMP stimulation and require mechanical trigger designs.

- Devices such as a bistable switches, linchpins or other "trigger" mechanisms should enable the desired SMP/piezoelectric interaction.

- Improvements in the recovery force available from SMP rods, sheets, foams or other structures are needed and will broaden the design possibilities.

SMP "Realities" and the Path Forward

- Formulation changes, incorporation of fibers, changes in foam density and shape optimization all offer means to improve the mechanical strength of SMPs.

- Combining heat (shape programming) and light (shape recovery) SMP behavior provides additional attractive and novel design options.

These challenges do not change the advantages that SMPs possess:

- large range of motion as compared to other polymer transitions or SMA materials such as Nitinol
- the use of both heat and light stimuli