

# Radiation Curing of 3-D Printable Polymers

Steven Shaffer<sup>2</sup>, Jim Amato<sup>3</sup>, Jonathan Reeder<sup>2</sup> and Walter Voit<sup>1,2,3</sup>



**Walter Voit**

McDermott Faculty

<sup>1</sup>Materials Science and Engineering

<sup>2</sup>Mechanical Engineering

**University of Texas at Dallas**

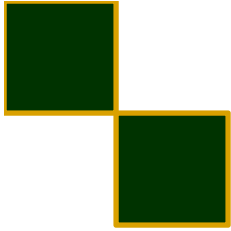
Chief Technology Officer

<sup>3</sup>Syzygy Memory Plastics



CIRMS 2012 – NIST – Gaithersburg, MD





# Background and Education

- BS in Computer Science from UT Dallas in 2005
  - Inaugural class of Eugene McDermott Scholars
  - Worked at Zyvex and Los Alamos National Labs
- MS in Intelligent Systems (Artificial Intelligence) from UT Dallas in 2006
  - Erik Jonsson Fellow
  - Advisor: I. Hal Sudborough
  - Thesis: “Pipeline: A software tool to improve the pancake problem upper bound”
- PhD in MSE from Georgia Tech in 2009
  - Presidential Fellow, TI:GER fellow
  - Advisor: Ken Gall
  - Thesis: “Optimization of mechanical properties and manufacturing techniques to enable shape memory polymer processing”

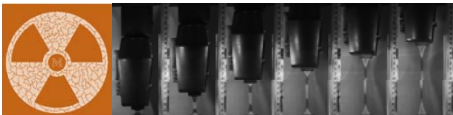




# UT Dallas Facilities – NSERL



**192,000-square-foot facility houses 350 faculty, graduate students and post-docs from electrical engineering, materials science, chemistry, biology, bioengineering and behavioral and brain sciences.**





# Cleanroom Facility (5000 ft<sup>2</sup> – class 10,000)

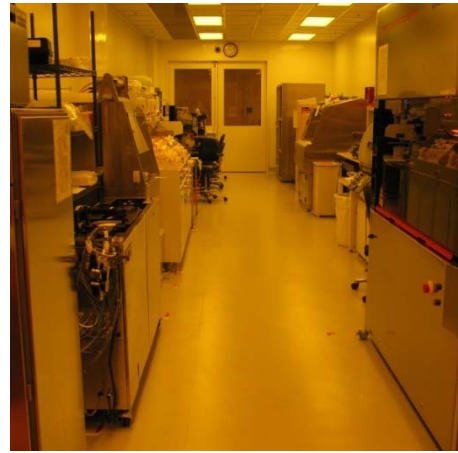
**Thermal Processing**



**Metallization**



**Photolithography**



**Wet chemistry**



**Characterization**



- Thin Film Deposition – LPCVD, PECVD, ALD, Sputter, Evaporation (e-beam and thermal)
- Etch – Deep RIE, metal etch, dielectric etch, silicon etch
- Thermal - Rapid Thermal Processing, oxidation
- Lithography - UV contact printing, e-beam, pattern, etch, laser mask writer, Nanoimprint
- Characterization - Electrical, physical, thermomechanical

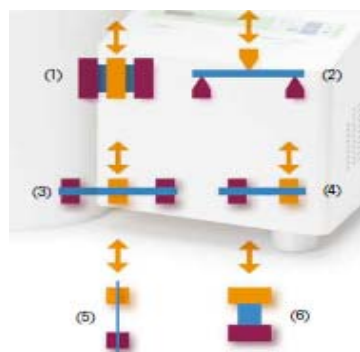


# Advanced Polymer Research Lab

## UT Dallas



Dynamic Mechanical Analysis



Deformation Modes



DMA Shear  
Clamp: Up to  
1000 Hz



DMA 3 point bend fixture – Load Cell: 40N, multi-frequency



Universal Testing Machine



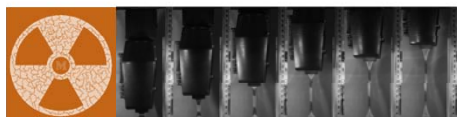
Differential  
Scanning  
Calorimetry

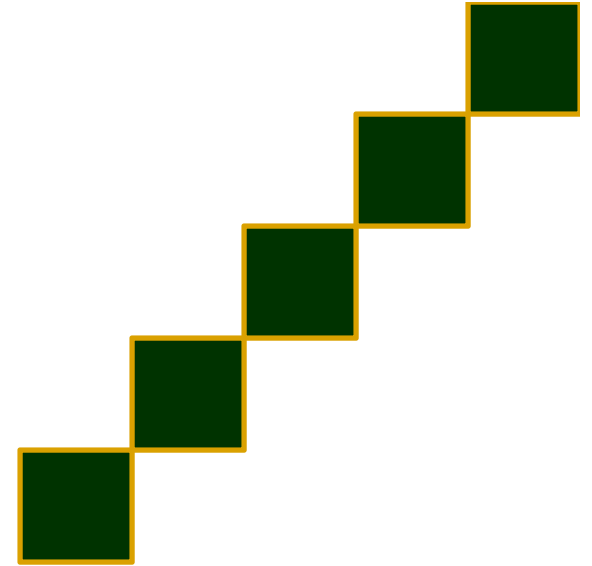


DSC Robotic Autosampler – Temp range -100 °C to 700 °C



Thermo Gravimetric Analysis





# COLLABORATORS & CONFERENCES





# Biomedical Device Laboratory



**BIOMEDICAL  
ENGINEERING**

Dr. Duncan J. Maitland



Keith Hearon



Dept. of Biomedical Engineering  
Texas A&M University





# Irradiation @ Nordion



CENTRE D'EXCELLENCE EN IRRADIATION  
GAMMA CENTRE OF EXCELLENCE

- World leader in gamma technologies
- Leading provider of Co-60
- Designs and builds irradiators
- Customers include:
  - Contract sterilization service providers
  - Medical device manufacturers
  - Product manufacturers



- [www.nordion.com](http://www.nordion.com)



# Advancing The Science of Irradiation

- A world-class applied research and specialty gamma process facility
- R&D focus at Nordion
  - Gamma Center of Excellence (GCE) and Science Sterilization team are part of the Global Research and Development Group at Nordion
  - Nordion mandate to advance the use of gamma irradiation technology



# Nordion's GCE vision



CENTRE D'EXCELLENCE EN IRRADIATION  
GAMMA CENTRE OF EXCELLENCE

- Grow the use of gamma through investment in research and innovation
- Seek collaborations with industry and academic partners
- Provide knowledge and training to the industry
- Develop talent and expertise in next generation of gamma professionals



- [www.nordion.com/gce](http://www.nordion.com/gce)



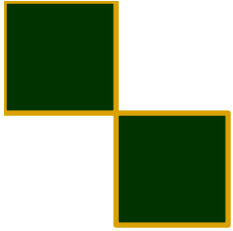
# International Meeting on Radiation Processing (IMRP) Shanghai, China early November 2013

**Chair:** Byron Lambert Chair

**Vice Chair of the Program Committee:** Wang Chuanzhen

**Chairman of the Organizing Committee:** Paul Wynne





# Technical Overview

- Bulk effects resulting from the interaction of shape memory polymers (SMPs) and ionizing radiation
- Independent control of glass transition temperature ( $T_g$ ) and rubbery modulus ( $E_R$ ) in polyacrylates
- 3-D printing and thermoplastic resins







# Acronyms

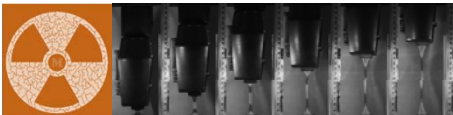
- Shape-memory polymer (SMP)
- Crosslinker (XL)
- Glass Transition Temperature ( $T_g$ )
- Rubbery Modulus ( $E_R$ )





# In-Hospital Device Manufacturing

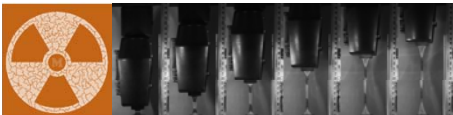
- Supply chain reliability in time of disaster
- Aim to allow hospitals to manufacture needed polymer medical devices
  - Infusion pumps for insulin, endo/laparoscopic device fittings, arthroscopic shaver handles



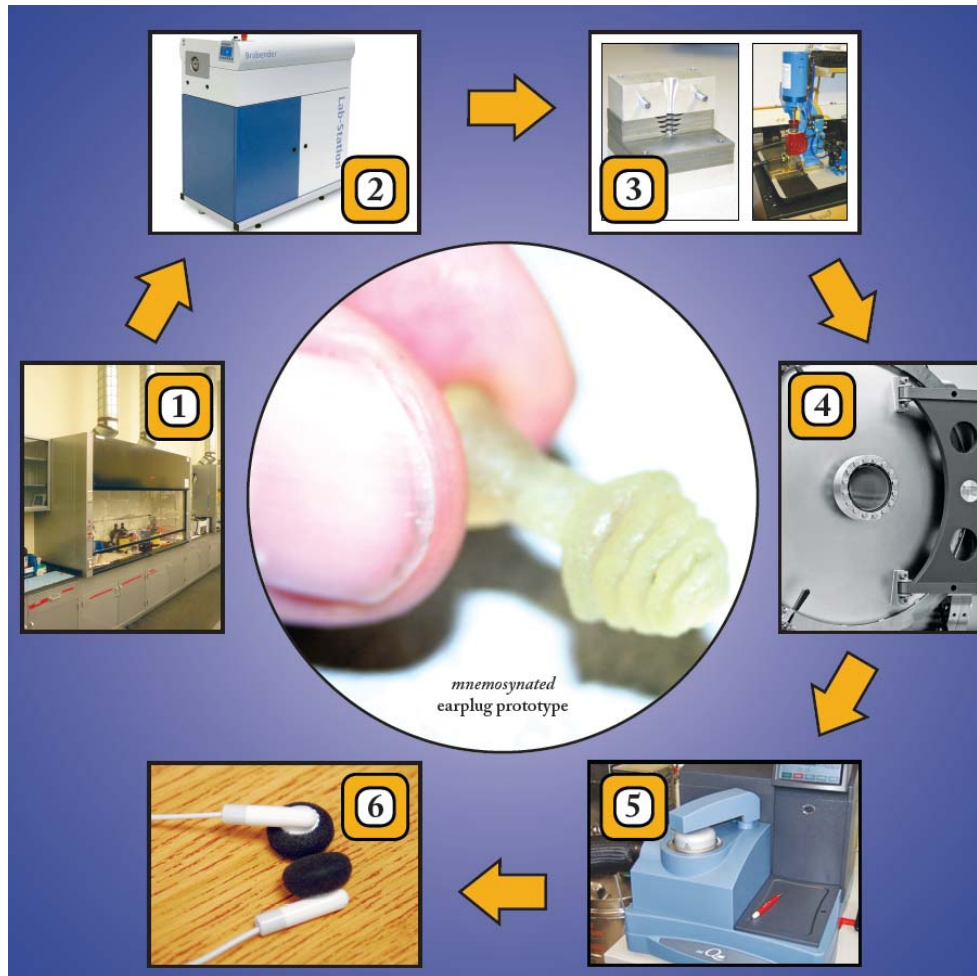


# 3D Printing

- Capability to rapidly manufacture devices
- Fused Deposition Modeling (FDM) printing requires low  $M_w$  polymer
- Many common FDM 3D printed polymers exhibit poor mechanical properties

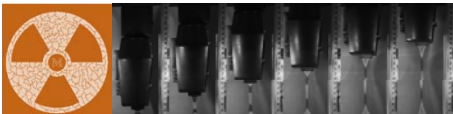


# Mass Manufacturing of SMP's

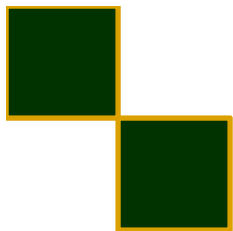


## Process:

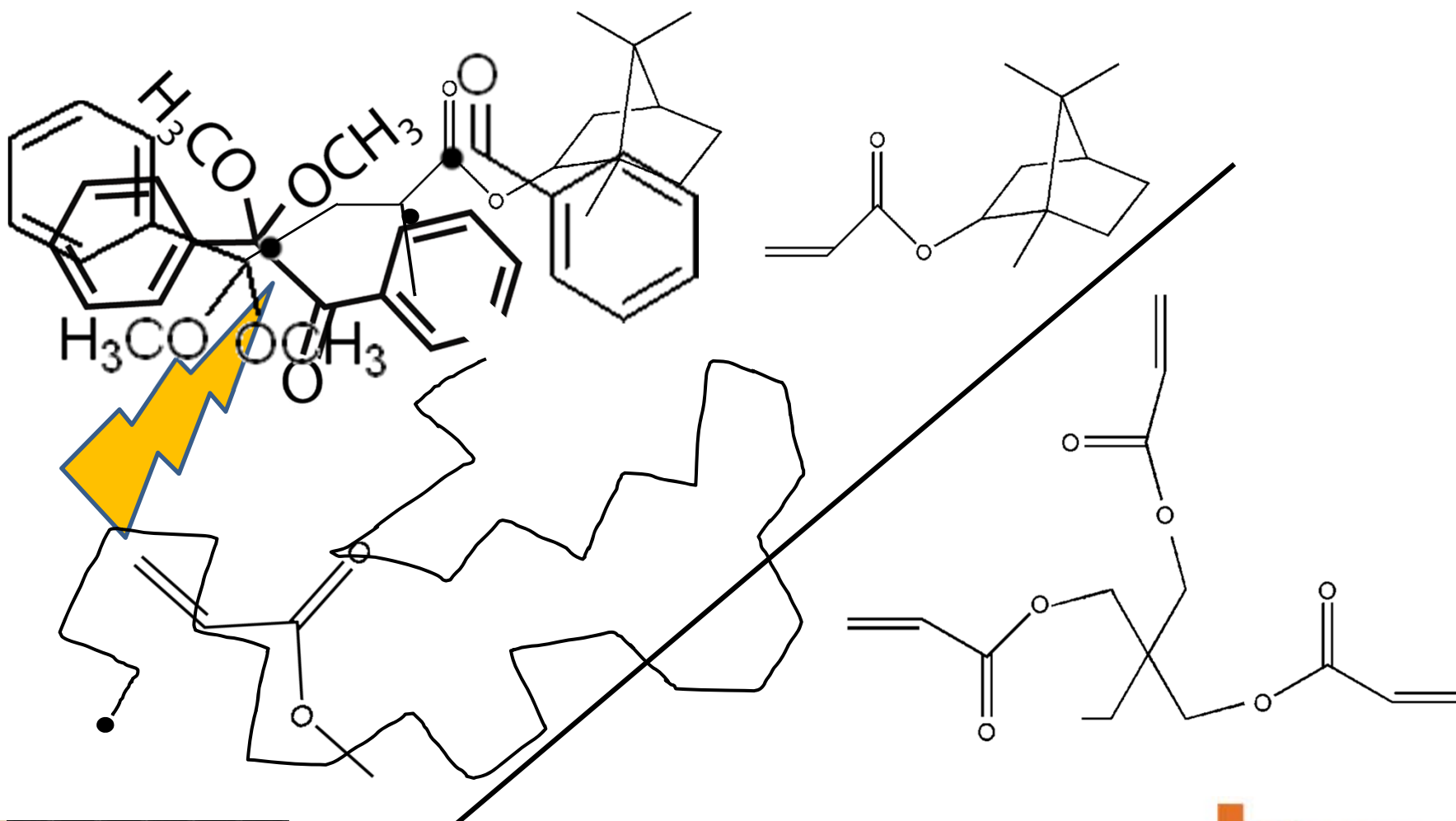
- 1.) tunable thermoplastic polymer synthesis,
- 2.) crosslinker blending,
- 3.) plastic molding and
- 4.) high-energy radiation
- 5.) to control final thermo-mechanical properties
- 6.) in a custom device.



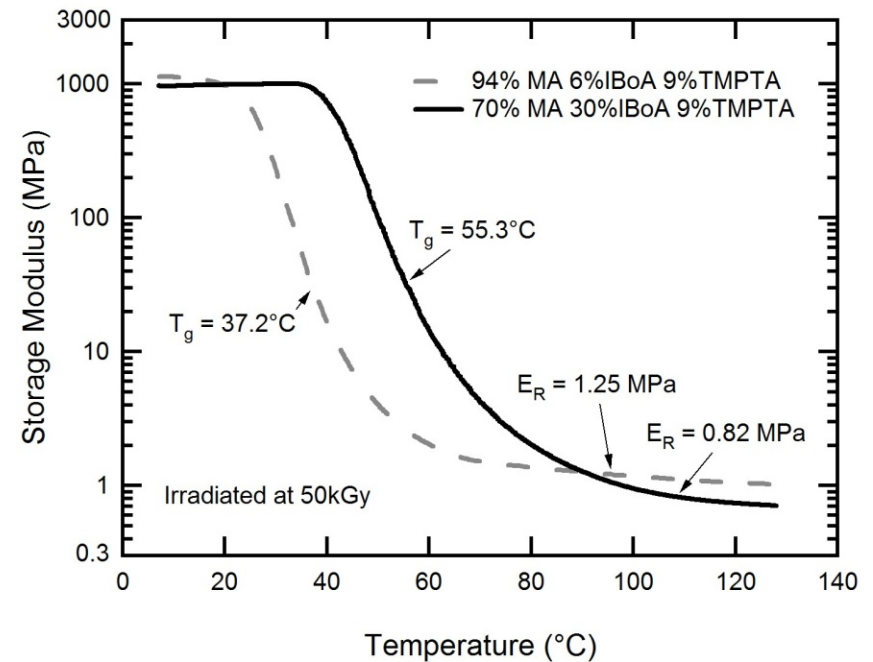
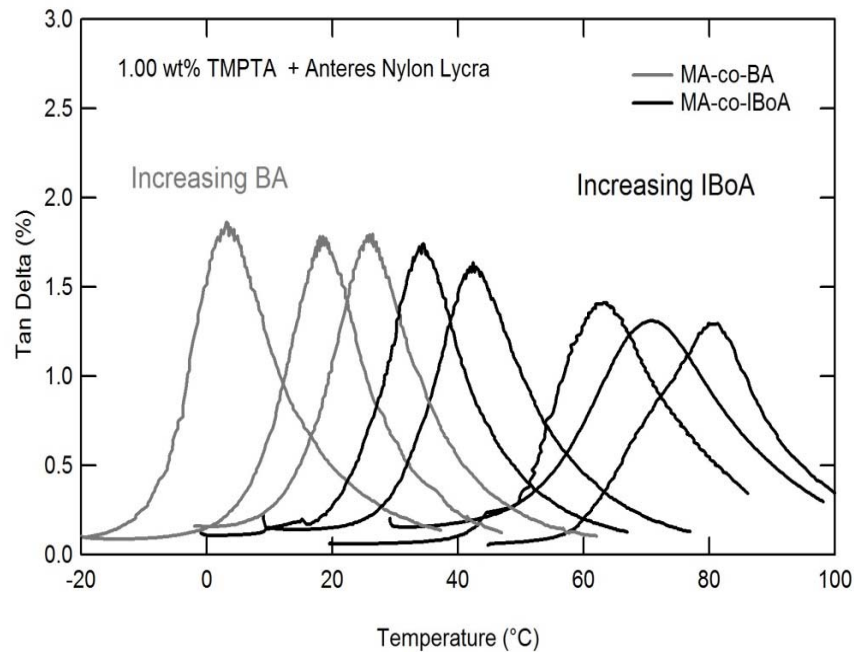




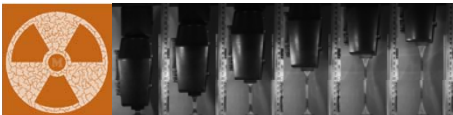
# Polyacrylate Polymer Synthesis



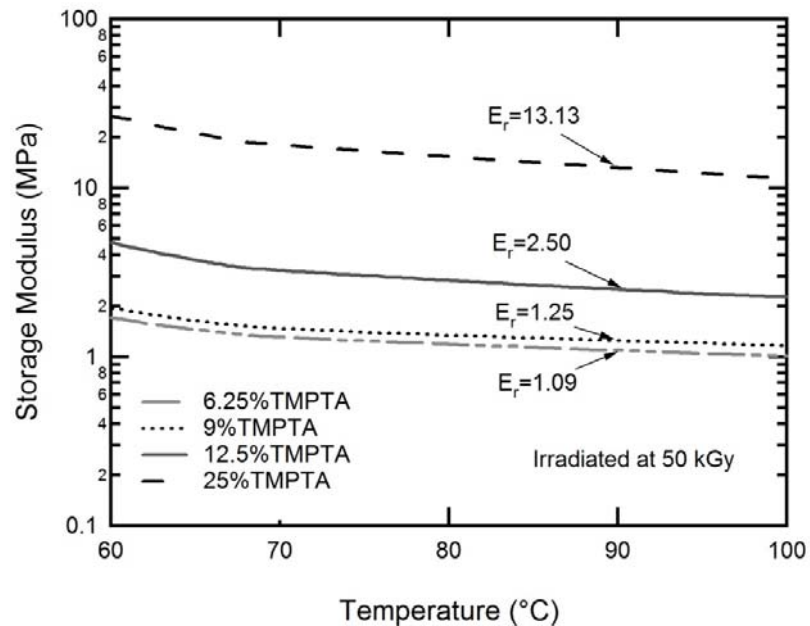
# Altering Glass Transition



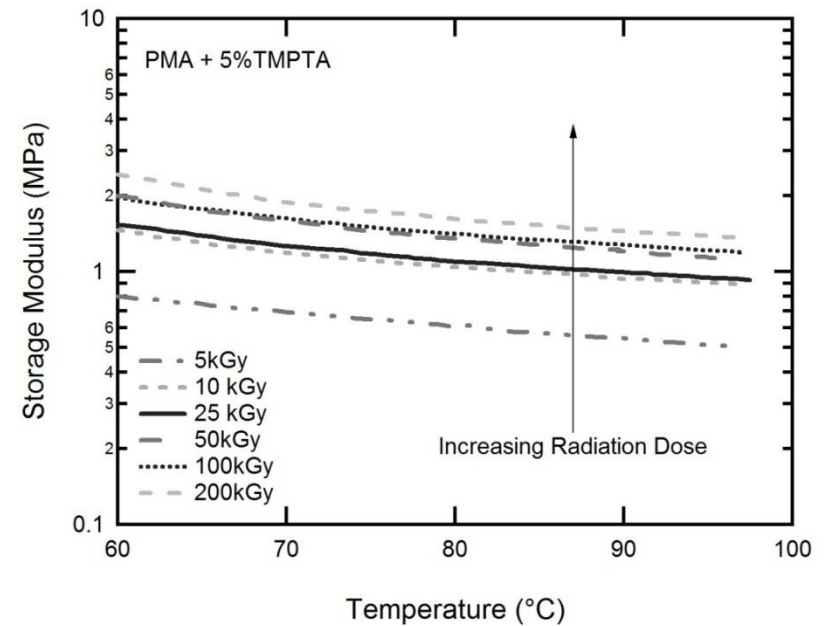
Ware, Ellson, Kwasnik, Drewicz, Gall and Voit (2011). "Tough Shape Memory Polymer Fiber Composites." J. Reinforced Plastics and Composites. **30**(5):371-380



# Altering Rubbery Modulus

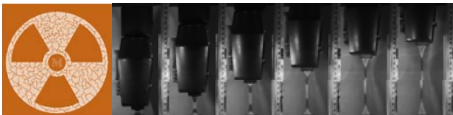


1. Changing crosslinker concentration



2. Changing dose

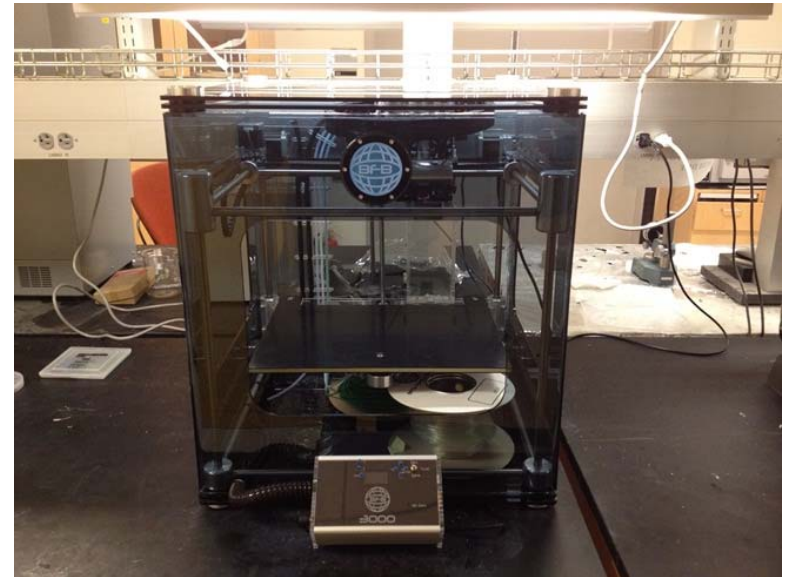
Voit, Ware, and Gall (2010). "Radiation Crosslinked Shape Memory Polymers." *Polymer*. **51**(15):3551-3559





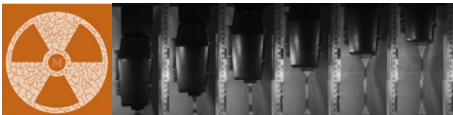
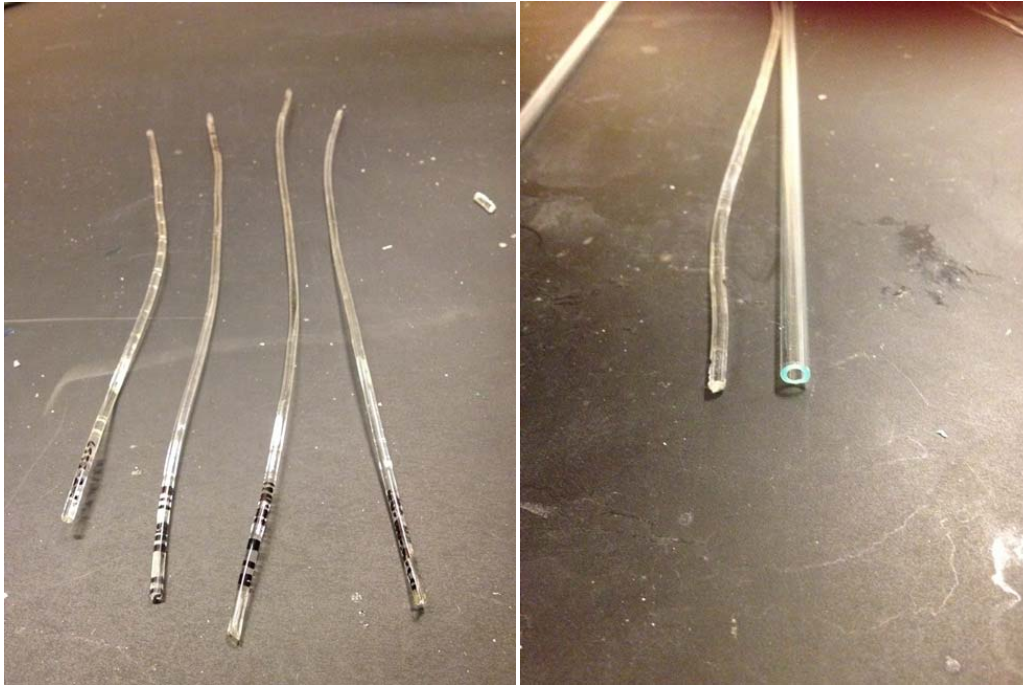
# 3D Printer

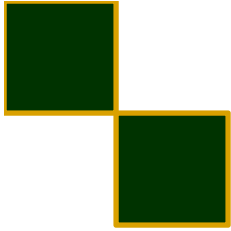
- BFB 3000
  - Fused Deposition Modeling
  - 3mm filament
  - Temp Range: 0°-260°
  - Feed Rate: 0-12.5mm/s
  - 0.5mm extrusion nozzle



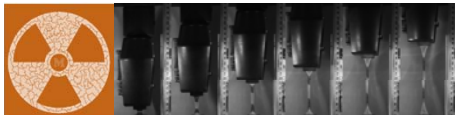


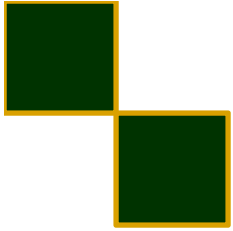
# Preparation of Thermoplastic resin





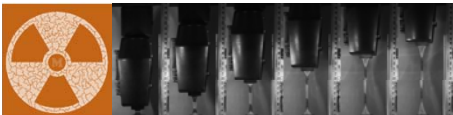
# 3D Printed Dogbone

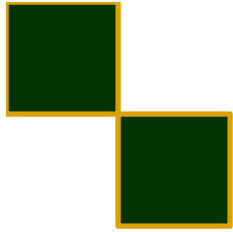




# Time/Temperature Resin Stability

- Inhibitor: Hydroquinone
- Prevents undesired crosslinker reactions due to heat or long storage time



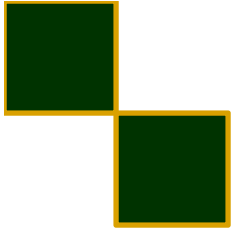


## Future Studies

- Can we understand the effects of temperature relative to the  $T_g$  on crosslinking?
- Can the effects of anisotropy in 3-D printed materials be reduced through post crosslinking by radiation?
- Will post-crosslinked, 3-D printed PLA and SMP composites add value for biomedical or other devices?



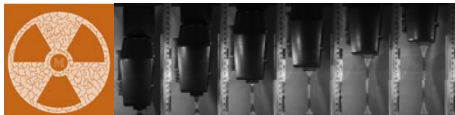




## Broad Impacts Today

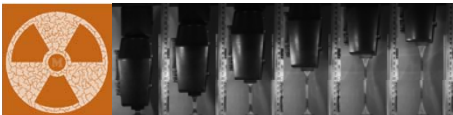
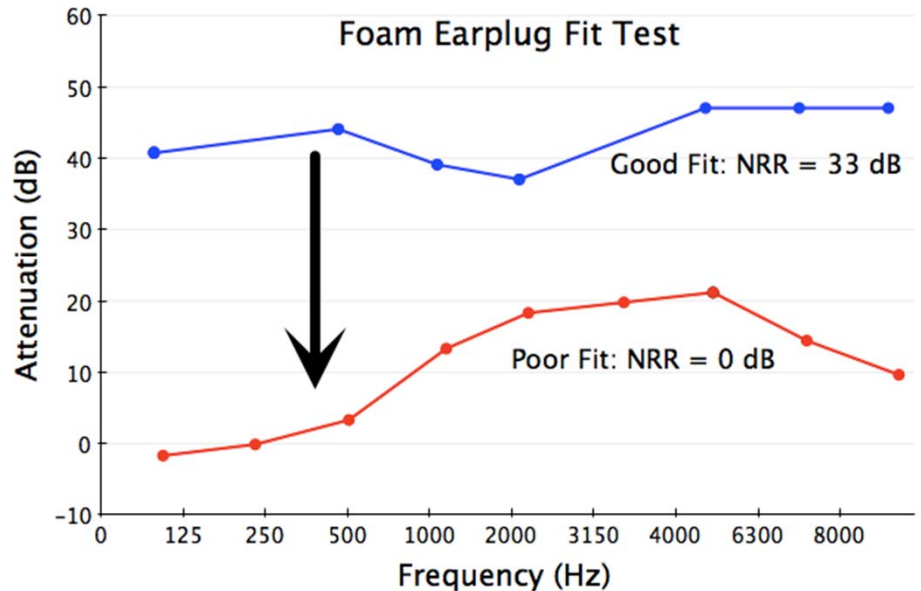
Syzygy Memory Plastics is developing the most advanced, effective, and comfortable hearing protection on the market.

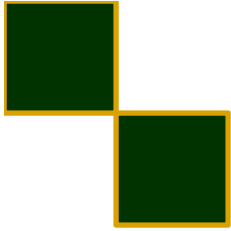
- Ineffective hearing protection is the leading cause of Noise Induced Hearing Loss (NIHL)
- NIHL is the **#1 occupational disorder** in the world, afflicting over 17% of all adults in the US with permanent damage to their hearing
- NIHL is **100% preventable** through better designed hearing protection.



# Technical Problems

- Current earplugs are inadequate
  - Not comfortable over long time periods
  - Users must choose sound attenuation vs. comfort
  - One size does not fit all, only fraction of users
  - Custom earplugs are expensive (\$100+) AND not dynamic
  - Insertion error -> poor fit -> ineffective sound attenuation





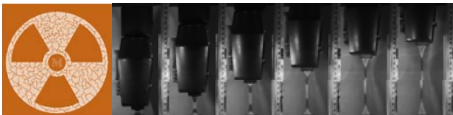
# Solution: PrēmEar Plugs<sup>TM</sup>

Unique, patented material and design that enables the following features, benefits and advantages:

- Heat activated material that creates a self-customized fit thus enabling more comfortable protection
- Dynamically comfortable to better seal the ear canal creating greater protection
- Simple to insert thus enabling a more fail-safe earplug to more effectively block unwanted sound
- Priced comparably to existing reusable earplugs, making comfort and high protection affordable to all users

## Insert

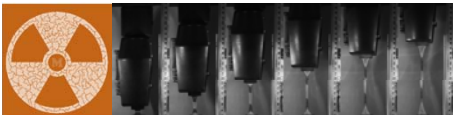
## Comfort

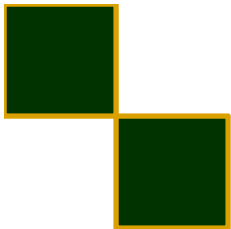




# Conclusions

- Devices can be crosslinked using ionizing radiation after manufacturing by 3-D printing
- $T_g$  and  $E_r$  are able to be tuned independently
- Poly (lactic acid) copolymers and blend can potentially serve as interesting components in 3D printing systems
- SMP earplugs are a near commercial demonstration of advanced polymer technologies





# Acknowledgements



- **Advanced Polymer Research Lab Post Docs (UTD):** Yuvaraj Haldorai, Wenzhe Cao
- **APRL Graduate Researchers:** Taylor Ware, Connie Manz, Dustin Simon, David Arreaga, Adrian Avendano, Jonathan Reeder, Tony Kang
- **APRL Undergraduate Researchers:** Abhishek Raj, Sagar Shah, Clive Liu, Ryan Marcotte, Courtney Keeler, Wesley Fichera, Lance Sweeney, Brayden Ware, Dimirti Porcelli, Cory Swanson, Vivek Raman, Joshua Olson
- **Syzygy Memory Plastics:** Dr. Brent Duncan, Taylor Ware, Jim Amato, Mike Moussa
- **Texas A&M:** Dr. Duncan Maitland, Keith Hearon
- **Mentors in the radiation community:** Mohamad Al-Sheikhly, Tony Berejka, Chip Starns, Eric Burgett
- **Georgia Tech/MedShape Collaborators:** Prof. Ken Gall, Prof. Chris Yakacki, Dr. Dave Safranski, Dr. Kathryn Smith
- **Corporate Collaborators:** Texas Instruments, Plexon, TriQuint, Syzygy Memory Plastics, Nordion, ScanTech Sciences
- **Academic Collaborators:** Drs. R. Rennaker, E. Keefer, M. Kilgard, D.W. Smith, R. Roeser, M. Quevedo, B. Gnade, S. Wagner, K. Wooley, B. Wester, Y. Hanein (and M. David-Pur), J. Elisseeff, H. Lu, D. MacFarlane, and S. Priya
- **Government Collaborators:** Drs. M. Di Prima (FDA), L. Karam (NIST),
- **Funding Sources:** UT Dallas, NSF IGERT grant 0221600, NSF Partnership for Innovation, **FDA Medical Countermeasures**, DARPA RPI (Plexon), Venture Lab 1803002 and 1803005, PURA grants, NSF SBIR 0912586 Phase I, Phase IB, and Phase II, McDermott Scholars Program, Syzygy Memory Plastics, FUSION, Center for Energy Harvesting Materials and Systems and the State of Texas

