Radiation Curing of 3-D Printable Polymers

Steven Shaffer², Jim Amato³, Jonathan Reeder² and Walter Voit¹,²,³

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Walter Voit
McDermott Faculty
¹Materials Science and Engineering
²Mechanical Engineering
University of Texas at Dallas

Chief Technology Officer
³Syzygy Memory Plastics

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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”
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 ft² – 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**
- DMA 3 point bend fixture – Load Cell: 40N, multi-frequency
- DMA Shear Clamp: Up to 1000 Hz
- Deformation Modes

**Differential Scanning Calorimetry**
- DSC Robotic Autosampler – Temp range -100 °C to 700 °C

**Thermo Gravimetric Analysis**

**Universal Testing Machine**
COLLABORATORS & CONFERENCES
Biomedical Device Laboratory

Dr. Duncan J. Maitland

Keith Hearon

Dept. of Biomedical Engineering
Texas A&M University
Irradiation @ Nordion

• 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
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

• 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
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\textsubscript{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

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?
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™

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
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