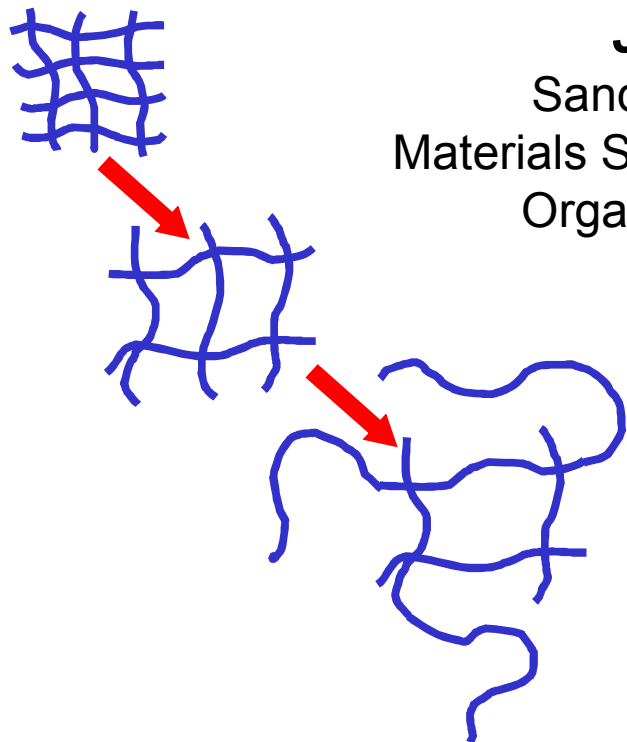


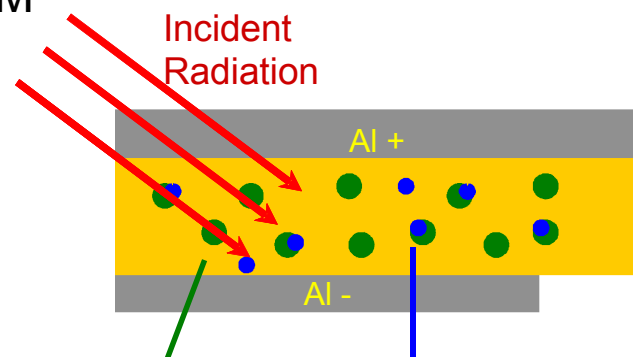
Polymer Science at Sandia National Laboratories: Fundamental Understanding to Practical Application

Joseph L. Lenhart

Sandia National Laboratories
Materials Science and Engineering Center
Organic Materials Department
Albuquerque, NM



1. Non-aqueous polymer gels



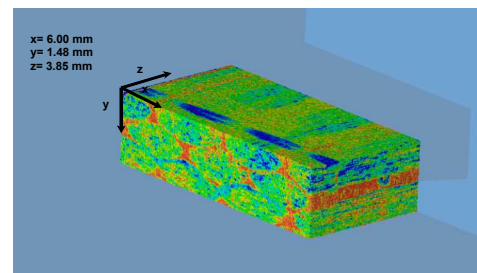
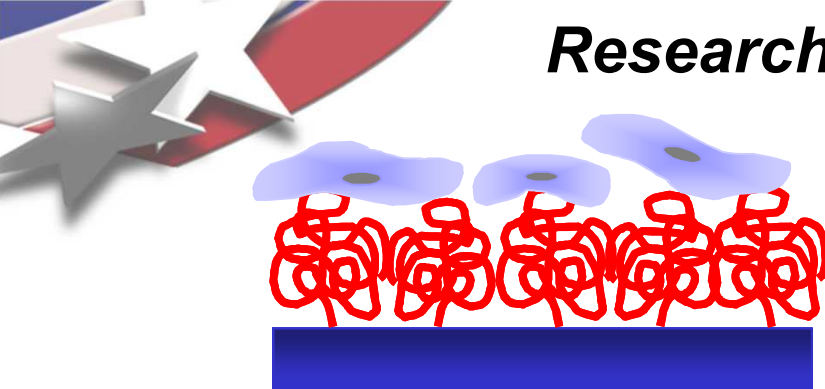
electron acceptor/donor
Incorporated in polymer as
a small molecule dopant

Radiation induced electrons
or holes captured by dopant

2. Radiation tolerant polymer films

This work was performed at Sandia National Laboratories. Sandia is a multiprogram laboratory operated by Sandia Corporation, a Lockheed Martin Company, for the United States Department of Energy's National Nuclear Security Administration under contract DE-AC04-94AL85000.

Research Background (Pre Sandia)

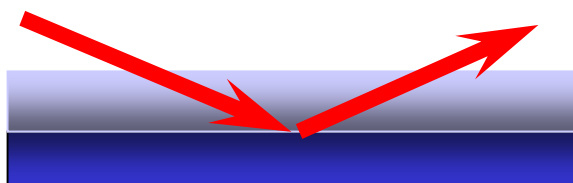
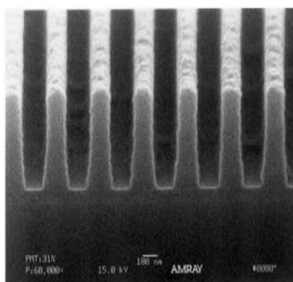


BS Chem E (UMBC)

- Bio-polymer chitosan
- Processing development
- Enzymatic reaction / chitosan absorption for water purification

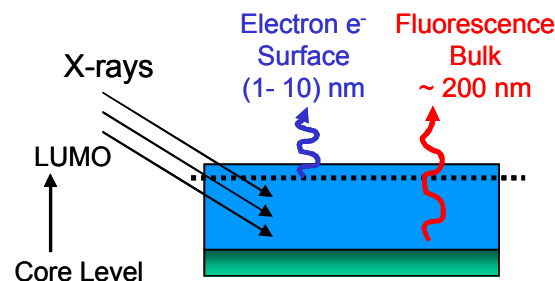
PhD Chem E (Johns Hopkins)

- Polymer composites
- Fluorescently labeled coupling agent
- Epoxy / silane / glass interface
- Fiber optic sensor



Neutron and X-ray reflectivity

- Thermal properties of ultrathin crosslinked polymer films

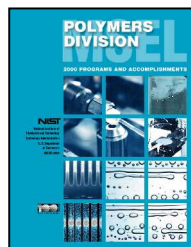


Interfacial phenomena in photolithography

- Led CRADA with Brewer Science
- Part of NIST / IBM team
- Resist-air interface
- Resist-BARC interface
- BARC thin film and surface characterization

Synchrotron Interfacial Science

- Polymer surfaces
- Interfacial chemistry of lithographic materials

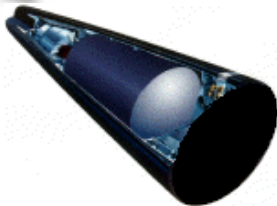


NRC Postdoc at NIST



Sandia National Laboratories

Sandia Mission Areas



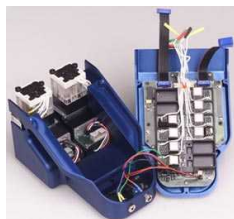
1) Nuclear Weapons

- Weapons surveillance
- New technology
- Maintain safe, secure, reliable stockpile
- Update weapons



Defense Systems and Assessment

- Science and technology development
- Missile defense
- System level simulation / computation
- Robotics
- C3ISR (Command, Control, Communication, Intelligence, Surveillance, Reconnaissance)



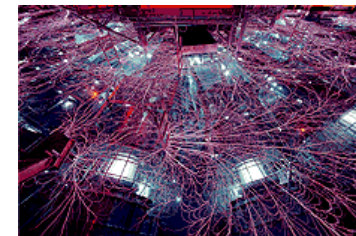
Nuclear Weapons Complex

- Los Alamos
- Lawrence Livermore
- Sandia (NM, CA)
- Pantex Plant
- Kansas City Plant
- Oak Ridge Y-12
- Savannah River Site



2) Non-proliferation

- Treaty verification
- WMD detection capability
- Physical security
- Nuclear materials management



Science, Technology, Engineering

- Physical, chemical, nano-science (CINT)
- Materials science
- Science in extreme environments (radiation, voltage)



Energy and Infrastructure Assurance

- Renewable energy
- Safe, secure, reliable infrastructure
- Safe, secure, sustainable water supply

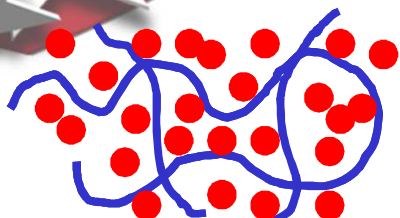
Homeland Security and Defense

- External partnerships
- Technology development i.e. detection, first responders, clean-up
- Manufacturability and commercialization

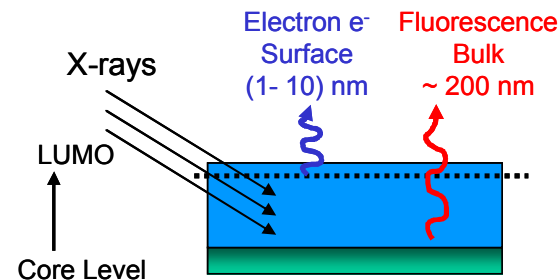
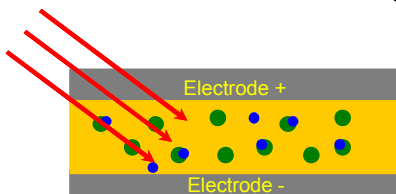
National
Security
Laboratory

Various Projects

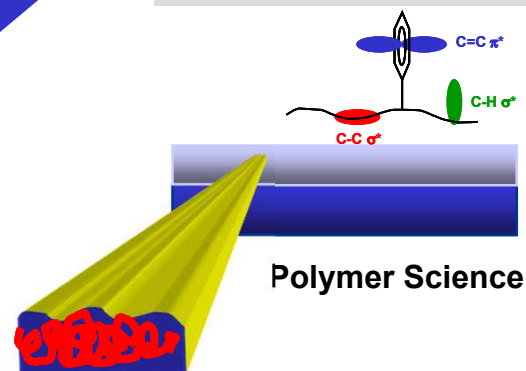
1) Soft Polymers / Gels / Elastomers



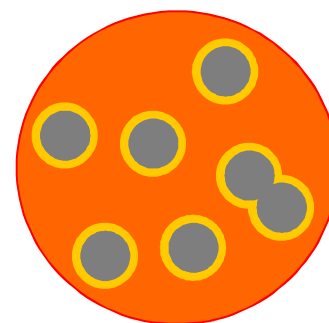
2) Radiation Tolerant Organic Materials



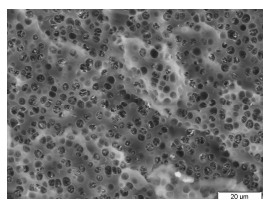
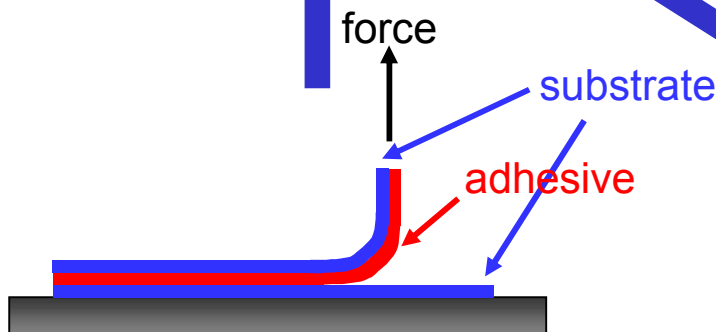
3) Thin organic films / interfacial characterization



4) Polymer Composites / Nanocomposites



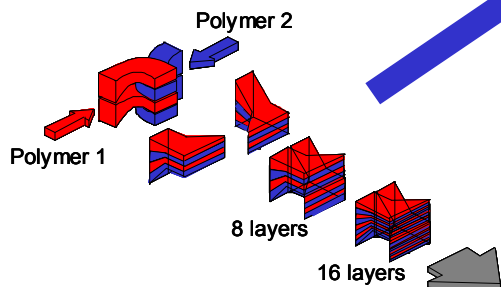
5) Polymer adhesion / adhesive and polymeric degradation



7) Polymeric materials for sensors



Multiplication Scheme



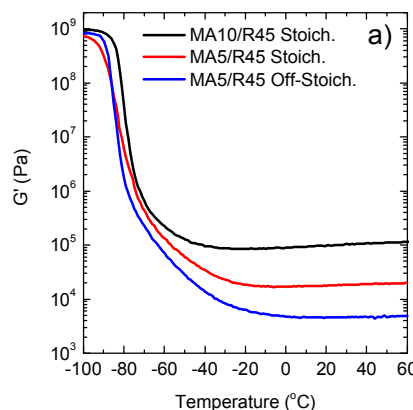
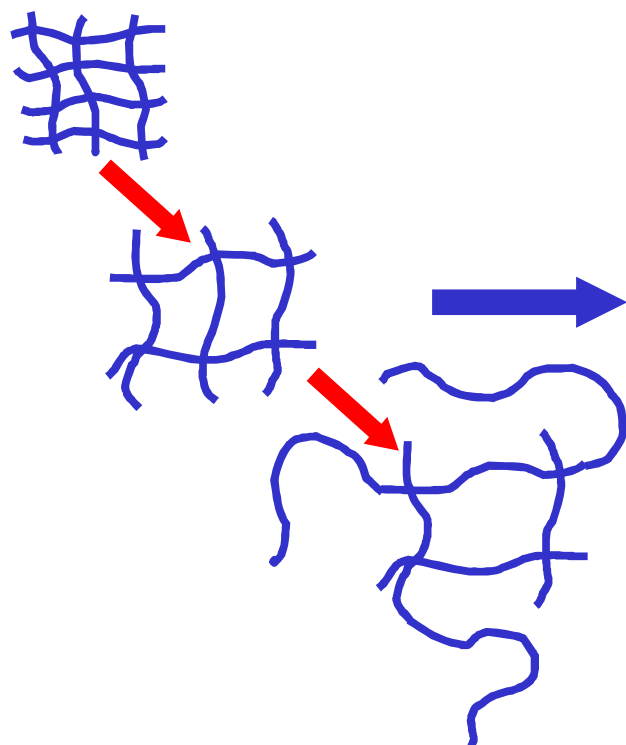
6) Multilayer Coextrusion

Joseph L. Lenhart (1821)



Sandia National Laboratories

Development of Non-Aqueous Polymer Gels for Electronic Devices and Sensor Applications



Chemistry and
microstructure

Material
performance

Process design and
implementation

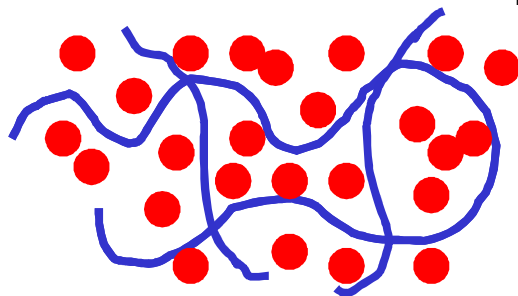


Sandia National Laboratories

Gel Technology Can Enable Various Applications

Tunability offers applications

- Polymer chemistry
- Solvent loading
- Solvent type
- Fillers / additives



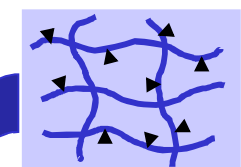
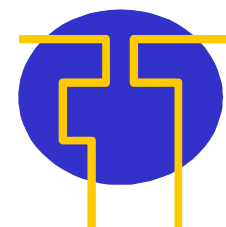
Objective: Design gels to perform over broad temperature range and lifetime.

- Flexible backbone
- Low volatility solvent
- No polymer or solvent transitions
- Polymer – solvent miscibility
- Good adhesion to a variety of substrates without surface preparation
- Adjustable reaction rate for various applications

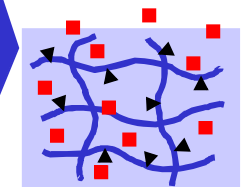
Impact

Sensors: Emerging national security concerns chemical / biological warfare and terrorism

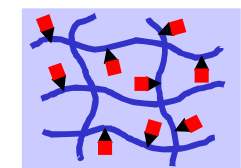
Current Applications: Electronic devices



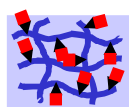
Highly swollen gel



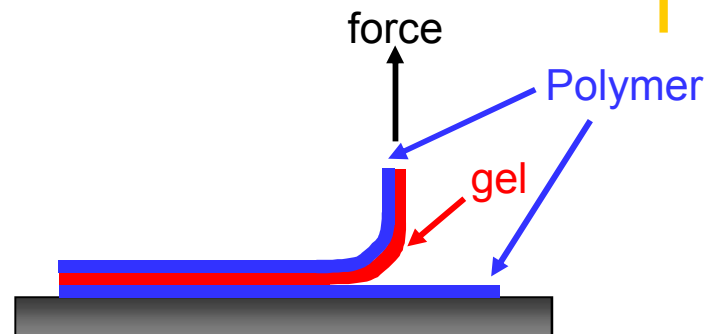
Analyte absorption



Analyte-receptor bonding



Gel shrinkage
And detection



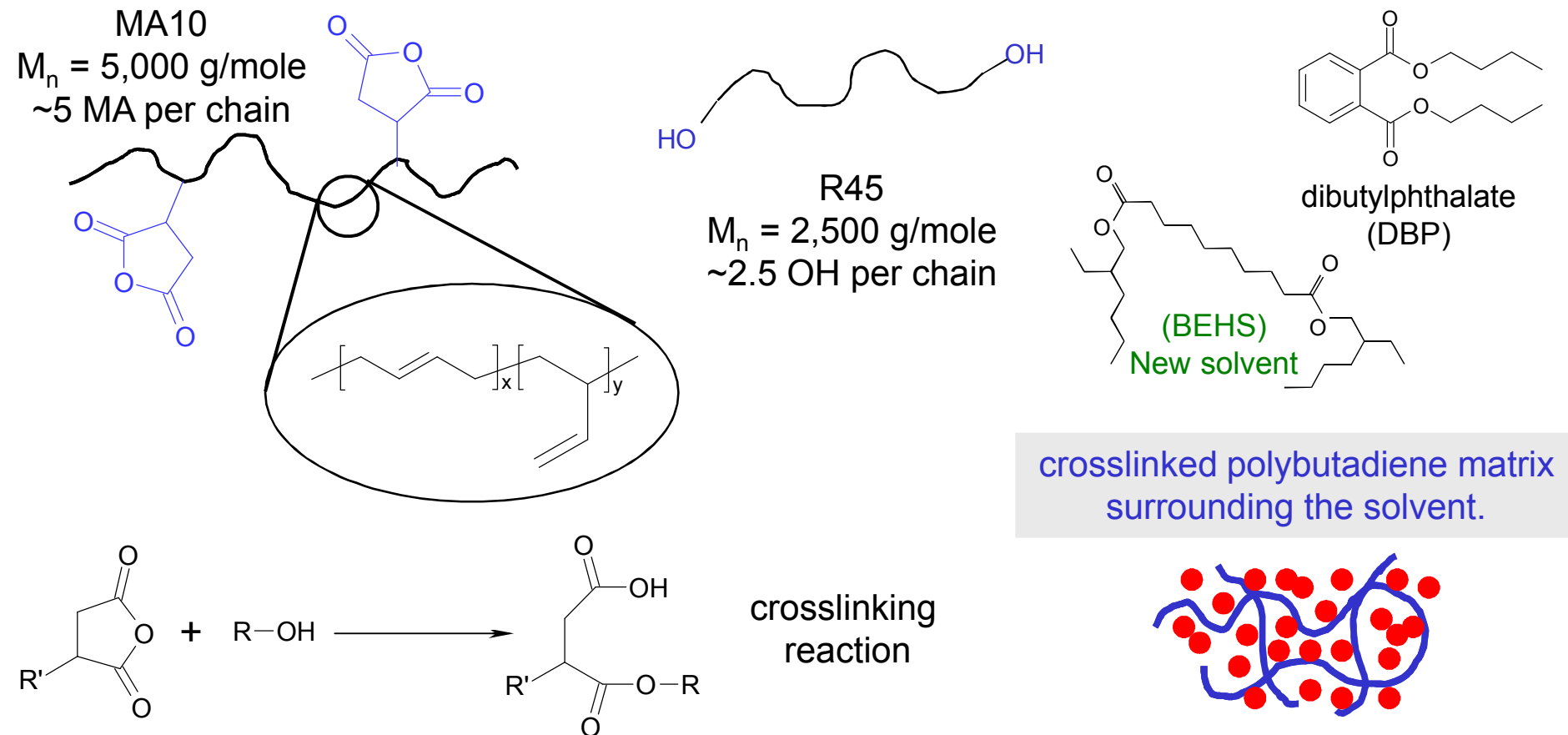
Gel – substrate adhesion is critical for device performance



Sandia National Laboratories

Initial Gel Formulation (MA10 Gel)

1. Assess whether the gel technology is feasible for a variety of devices
2. Develop materials solutions for functional devices
 - 4 months to make recommendation
 - Broad temperature requirements (-70 to 100°C)
 - Long lifetime requirements (30+ years)

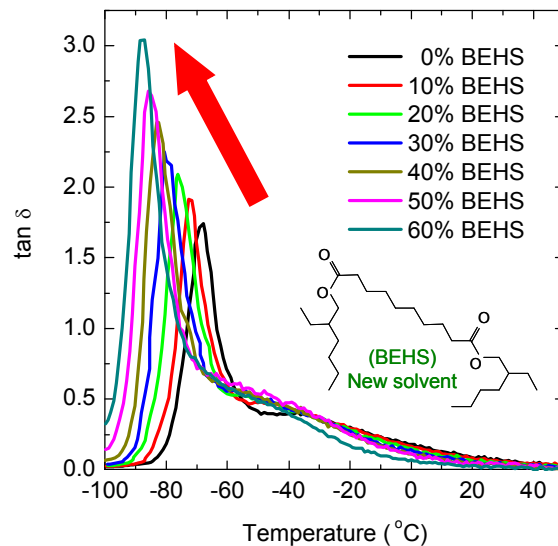
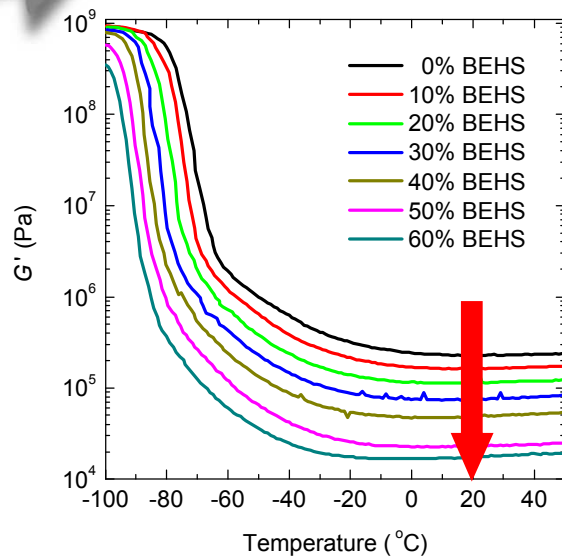


Crosslinking Reaction (promoted with tertiary amine catalyst)



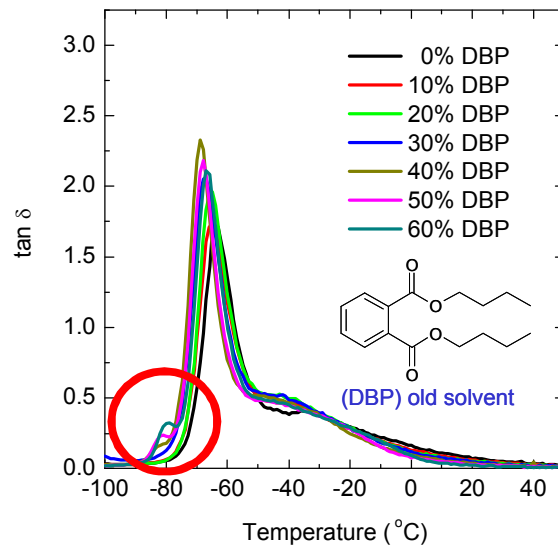
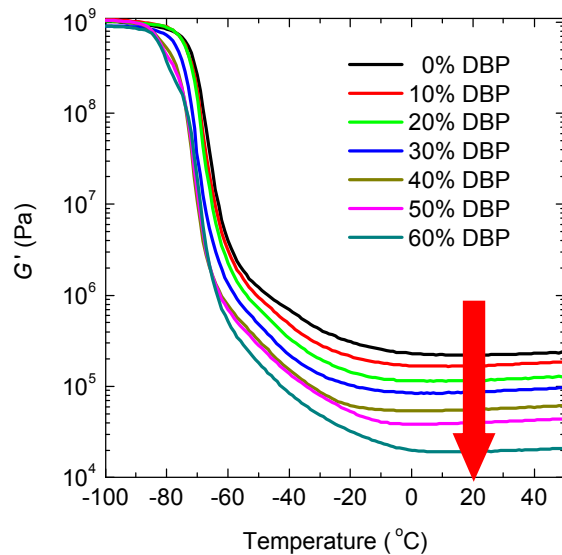
Sandia National Laboratories

Solvent Impact on Mechanical Properties



- Plateau modulus at $T > -40^{\circ}\text{C}$
- Increase in solvent content suppresses modulus and T_g

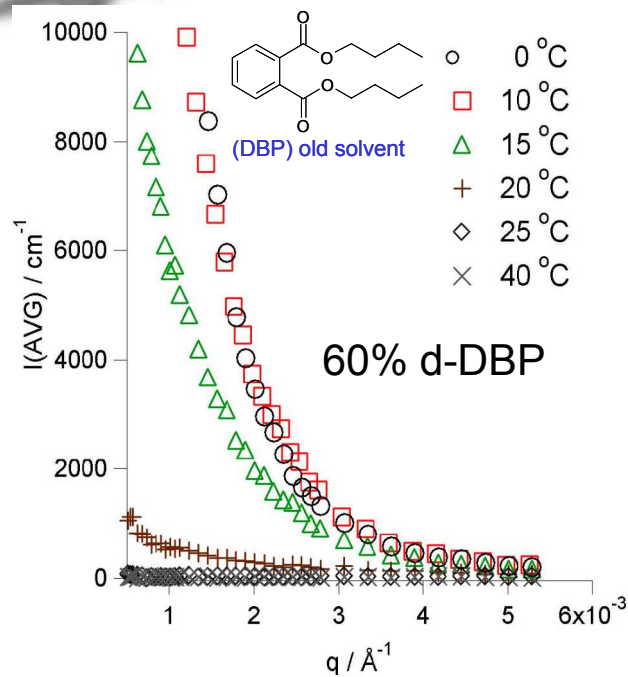
Need solvent that exhibits a maximum in swelling to provide broad temperature performance



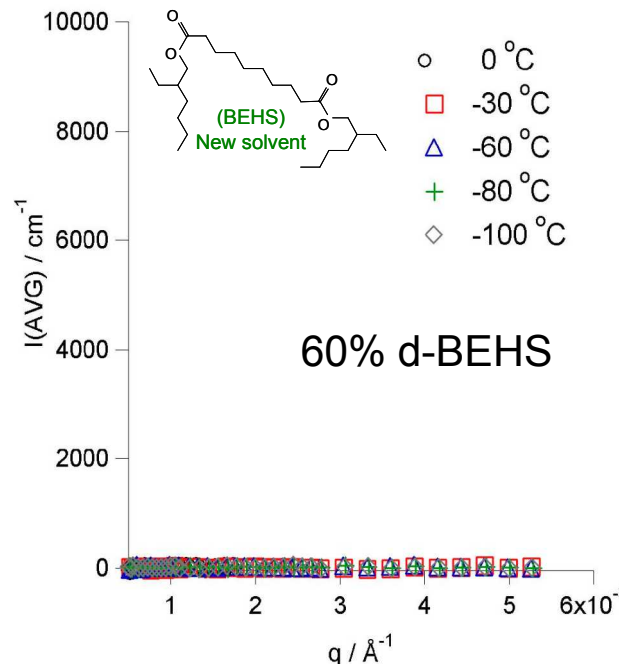
- Plateau modulus at $T > -10^{\circ}\text{C}$
- Modulus suppression with increasing solvent
- Phase separation with increasing solvent

Neutron Scattering

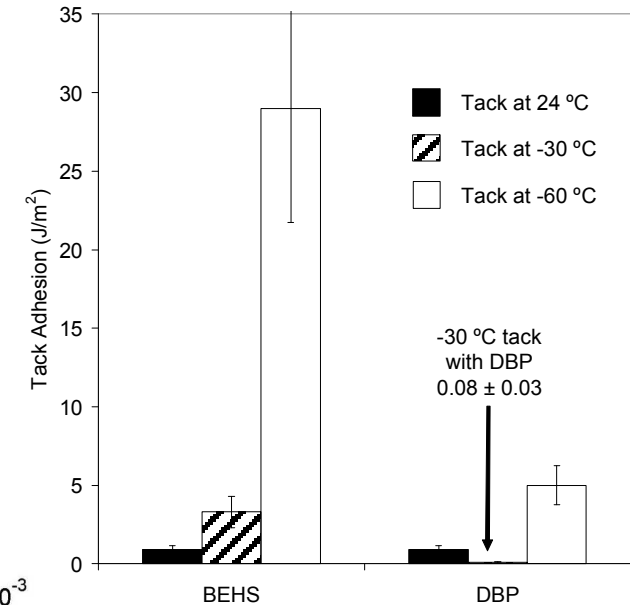
Prof. Ronald Hedden
Penn State Univ.
Materials Science Dept



- Strong scattering temperature dependence
- 60% DBP phase separates below 20 °C
- 80% DBP phase separates below 60 °C

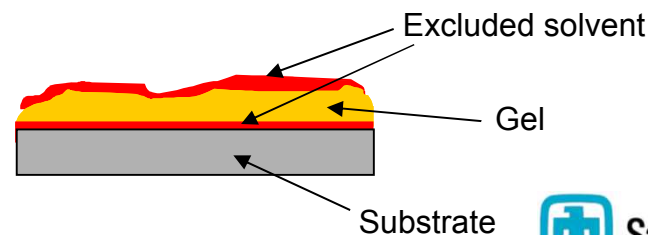


- No scattering temperature dependence
- 60% BEHS gels miscible even at -100 °C

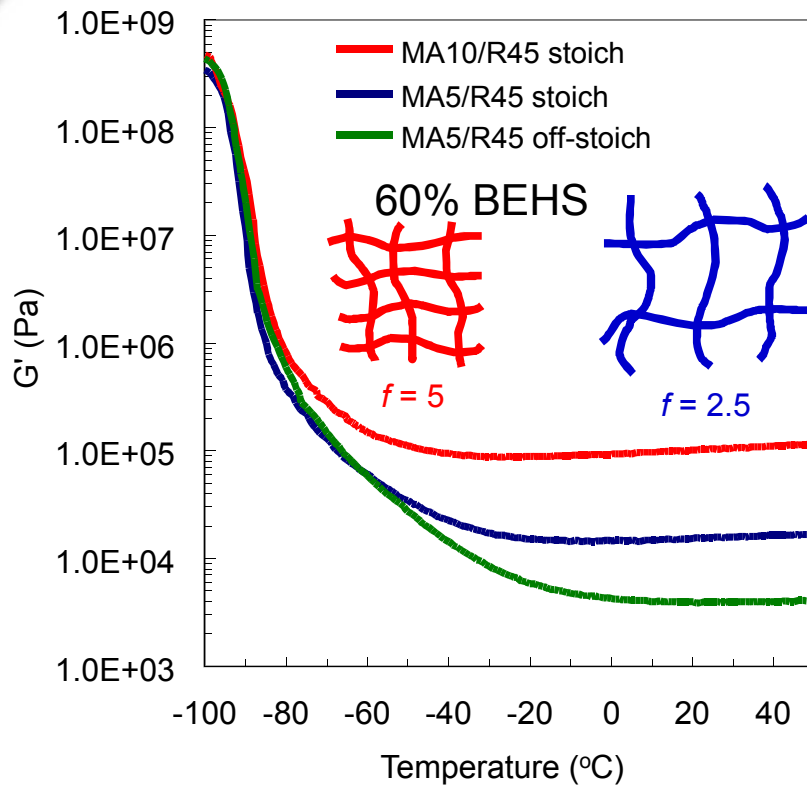


- Tack adhesion degrades with phase separation
- Devices fail due to gel delamination at critical interfaces

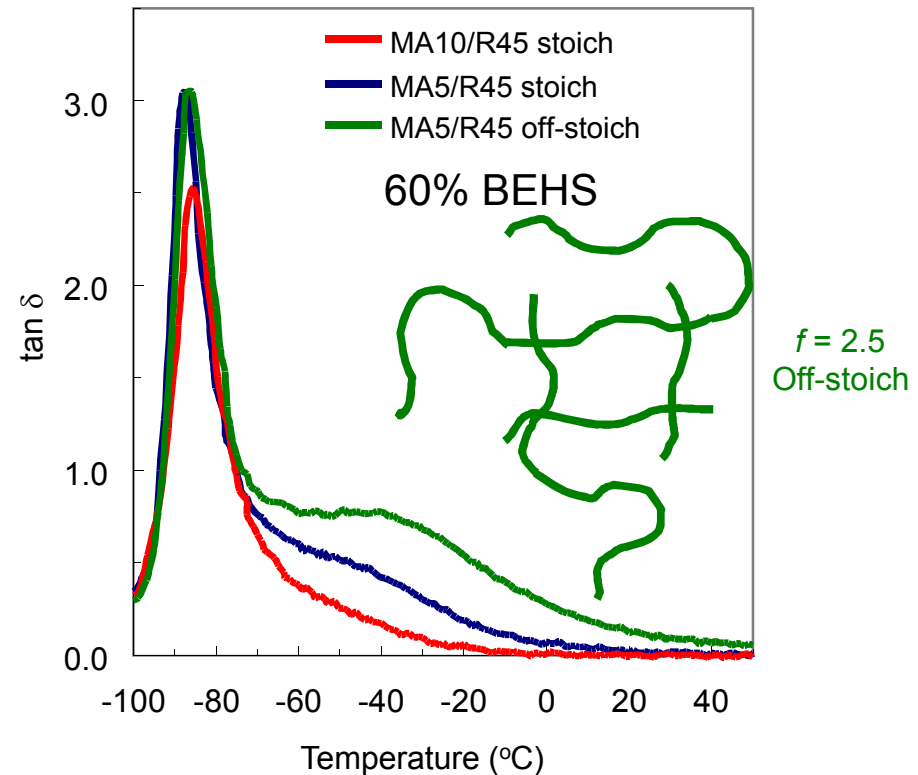
Switching to a solvent miscible over the device operating temperature range resulted in dramatic improvements in device performance



Impact of Cross-link Density



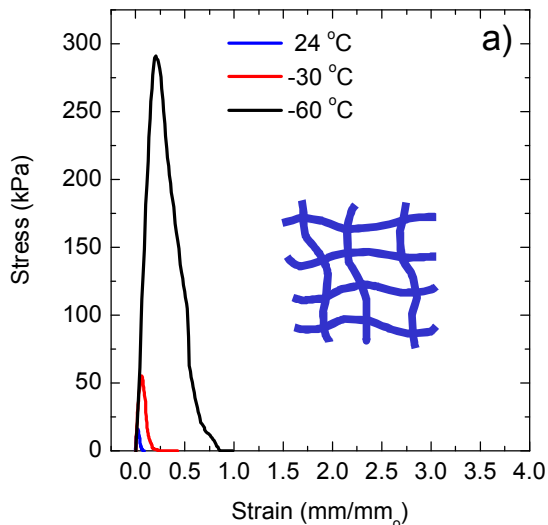
- Decreasing crosslink density decreases plateau value (reduced functionality, offstoichiometry)
- T_g identical
- Extractables equal at $61.5 \pm 0.5\%$



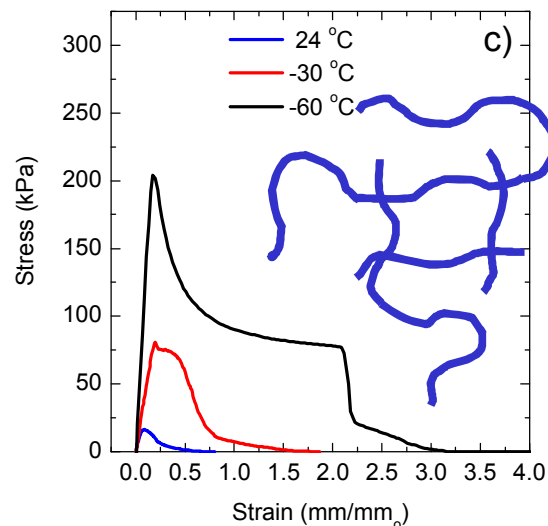
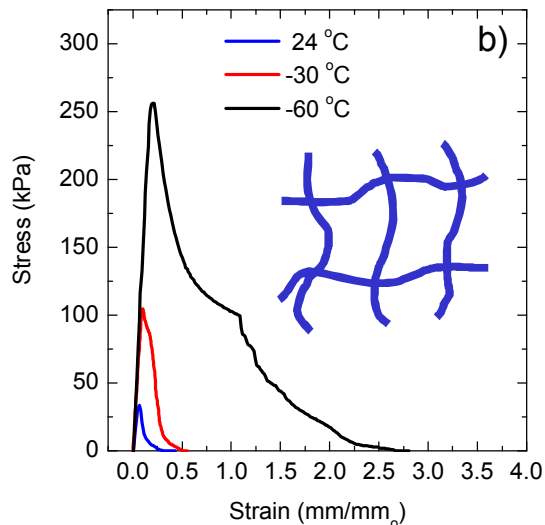
- Similar loss tangent behavior
- Increase in loss tangent (0 to -70 °C) with decreasing crosslink density
- Defects in the gel structure? ie. dangling ends

Correlation with Stress-Strain Diagrams

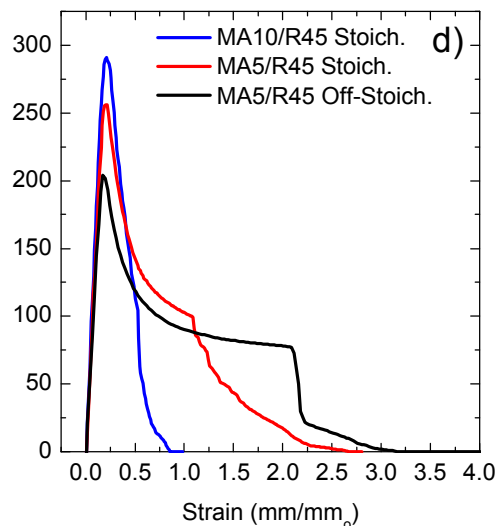
MA10 stoichiometric



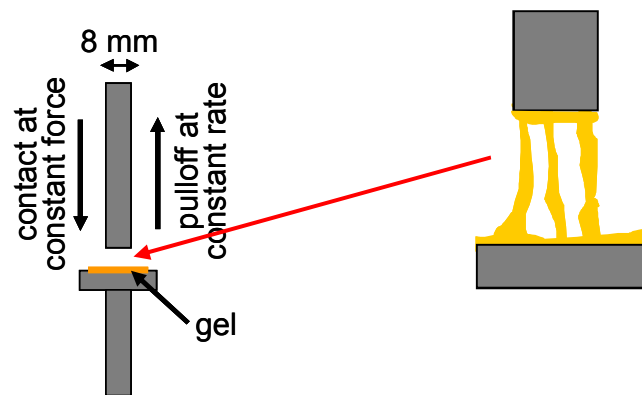
MA5 stoichiometric



MA5 off-stoichiometric



Comparison at -60 °C

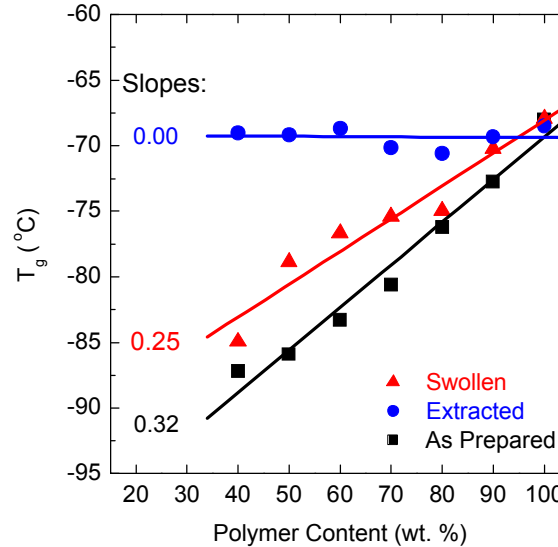
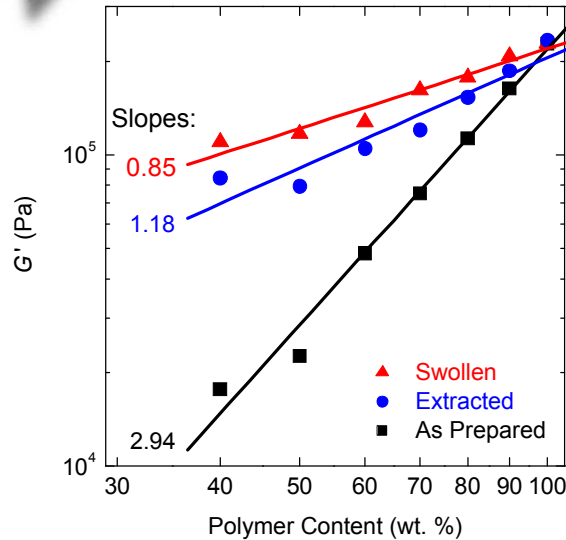


- As temperature decreases maximum and area increase (consistent with increasing loss tangent)
- As crosslink density decreases extension increases at all temperatures
- MA10 gels fail elastically even at low temperatures (small loss tangents)
- MA5 gels exhibit extension and fibrillation (high loss tangents)
- Similar behavior observed in non-swollen elastomers



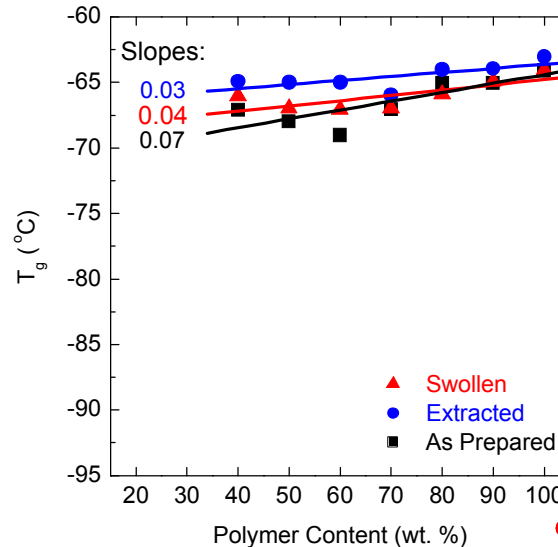
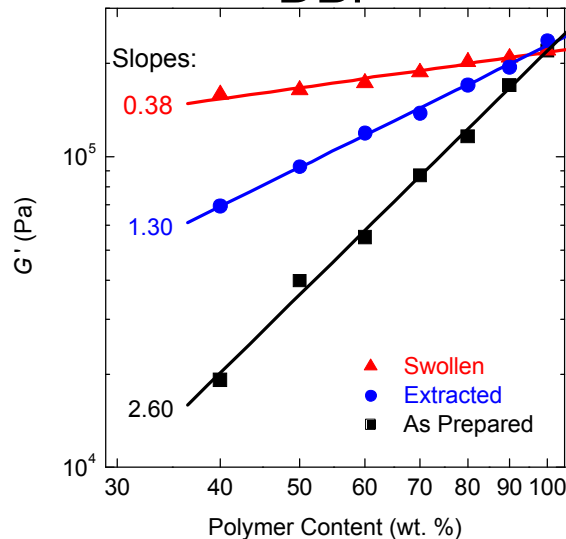
Processing Impact on Effective Crosslink Density

BEHS



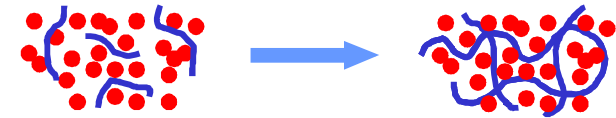
1. Different processing approaches required for various applications
2. As solvent loading increases in "as prepared" gels the entanglement density decreases
3. Processing (micro-structure) has bigger impact on properties than solvent loading
4. Entanglements do not impact elastomer T_g

DBP



Black – "As Prepared"

Mix polymer and solvent and cure together



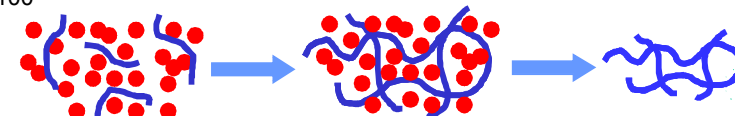
Red – "Swollen"

Cure polymer without solvent and swell to the desired solvent loading

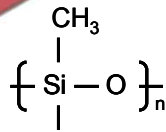


Blue – "Extracted"

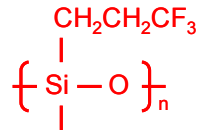
Cure polymer and solvent together and extract solvent leaving elastomer



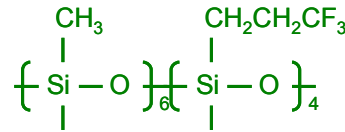
Transition to Silicones



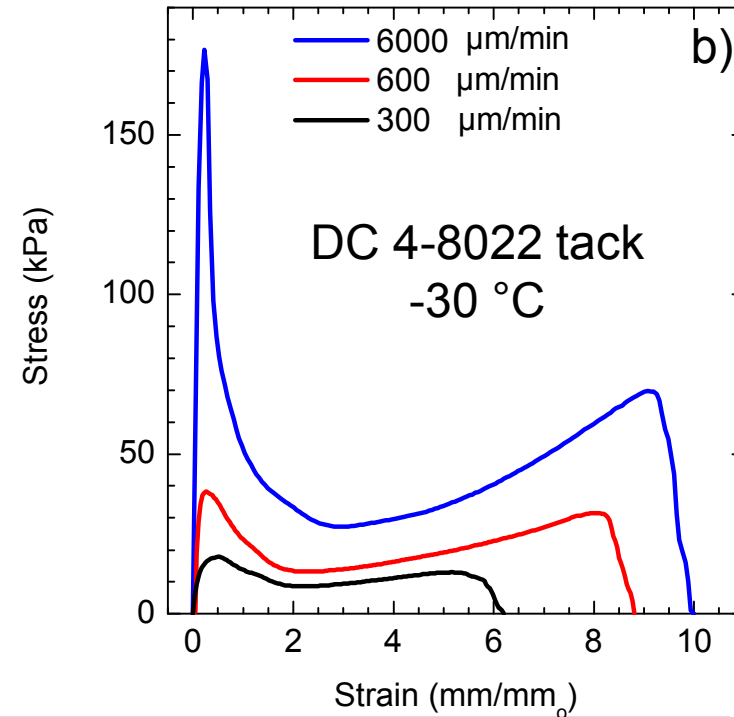
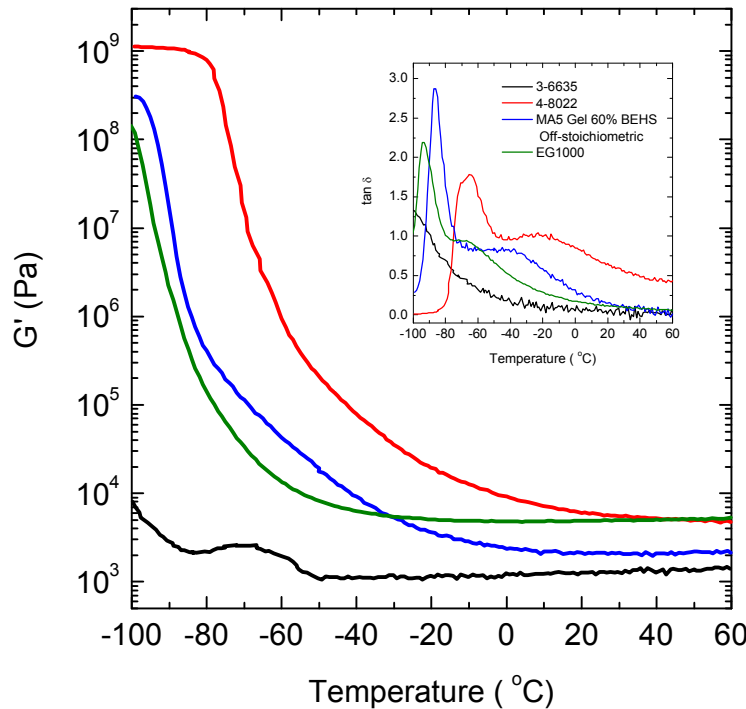
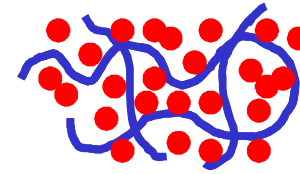
DC 3-6635



DC 4-8022



EG 1000



1. Polybutadiene gels will not meet lifetime requirements
2. Silicones have excellent chemical stability over device operating range
3. Copolymer and fluorosilicone gels exhibit:
 - High sol content
 - Plateau region $G' < 10^4$ Pa
 - High value for low temperature $\tan \delta$
 - Extension and fibrillation in tack testing
4. Excellent performance in device testing



Silicone – PBD Gel Comparison

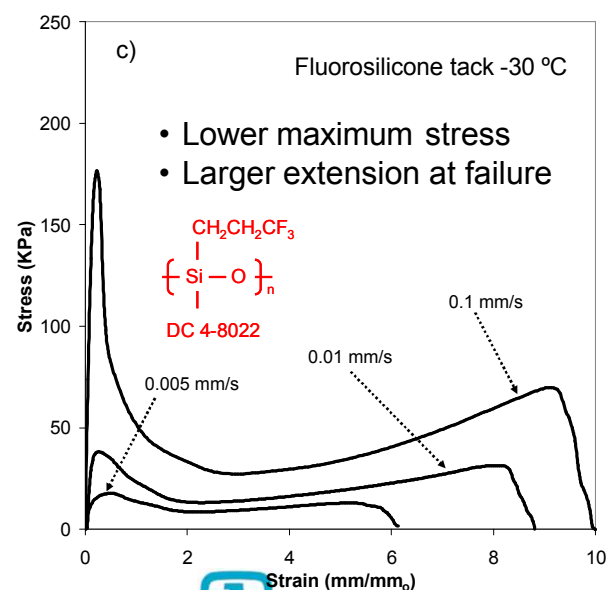
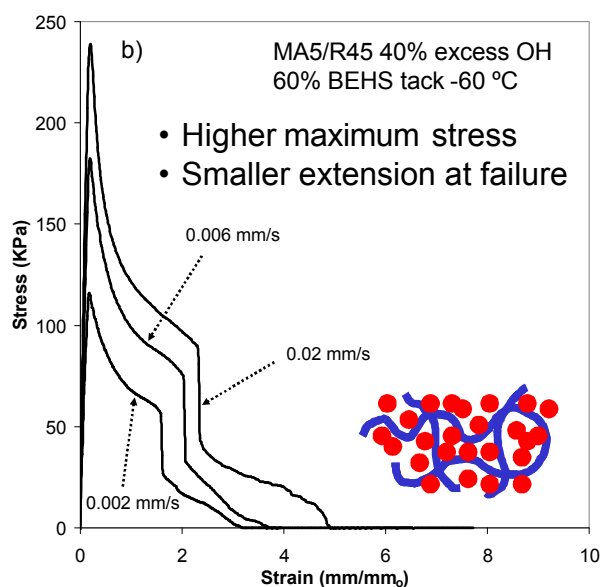
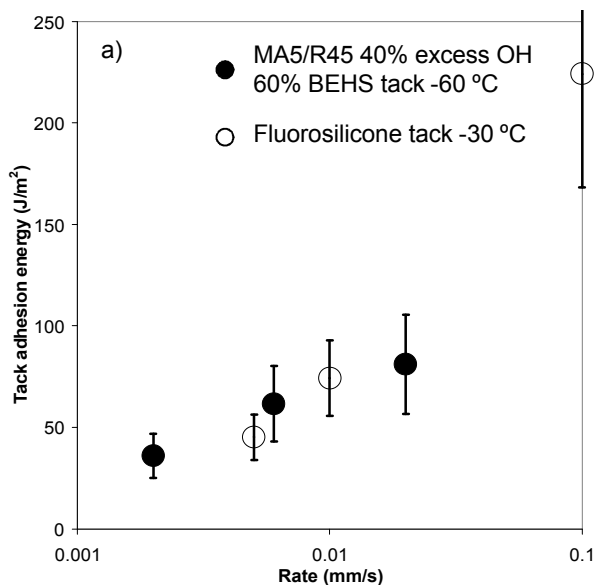
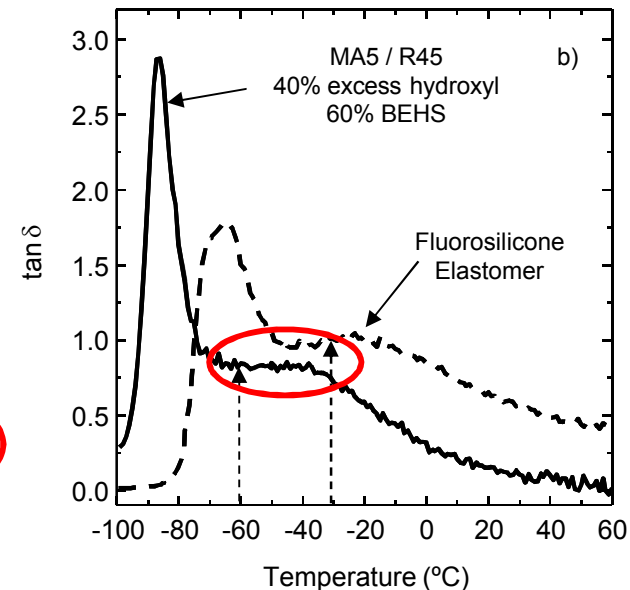
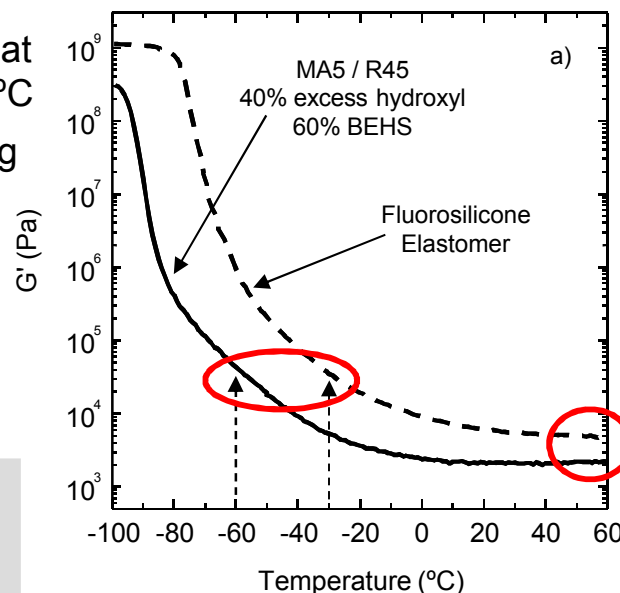
1. Compare fluorosilicone elastomer at -30 °C with BEHS/PBD gel at -60 °C

- Same temperature relative to T_g
- Same G' at temperature
- Same $\tan \delta$ at temperature
- Same plateau G'
- Same sol fraction

2. Same tack adhesion energy (integral of stress-strain)

3. Very different stress-strain shape

4. Is this due to large sol size in fluorosilicone gels?



Processing Development

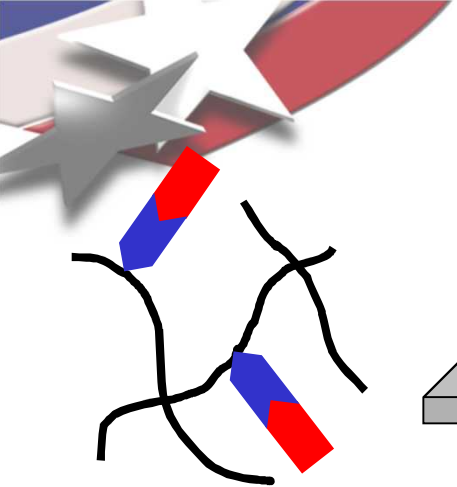
- Designed gel materials for functional devices
- Designed processing capability (small lab-scale, pilot scale, full production scale-quality processing)



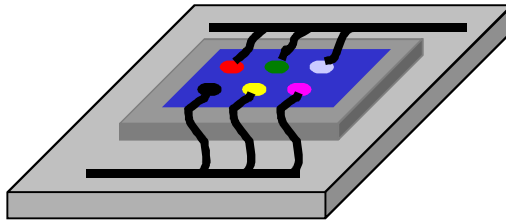
- 2 months to prove silicone viability
- 3 weeks to go from lab-scale (5 parts) to pilot-scale (50 parts)
- 5 weeks of processing and performance evaluation in devices
- 6 months to go from pilot-scale to fully automated production-scale (3 reaction vessels ~ 250 parts each) including testing and verification of device performance
- Transferred technology to an external vendor
- Lab-scale to production in < 1 year



Alternative Applications



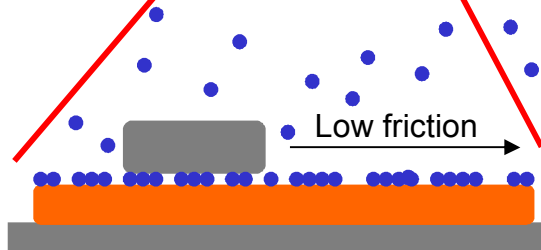
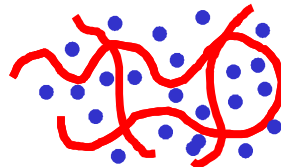
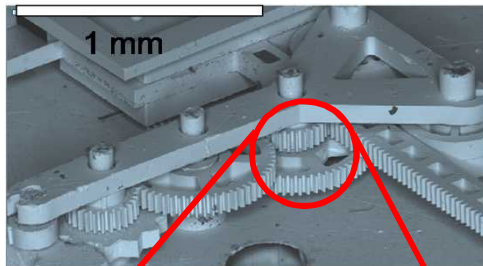
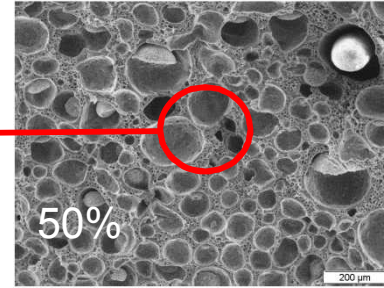
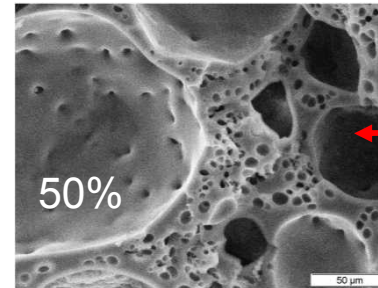
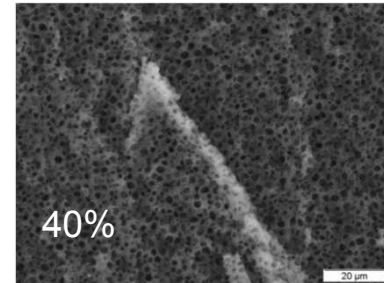
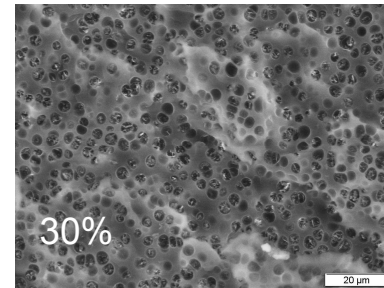
Develop specific agent
– receptor binding sites



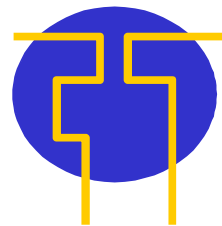
Develop functional
sensor devices / arrays

1) Sensor Opportunities

- Changes in equilibrium swelling
- High porosity scaffolds and “molecular templating”



2) Self-Healing Lubrication Layers

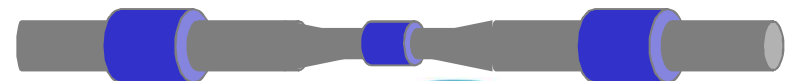


3) Stretchable
electronic
circuitry

4) Micro-devices / Soft Actuators Flexible Robots

Utilizing dispersed particle
allows large scale gel
deformation in response to
external fields

Micro-scale pumps, valves, switches, motors
driven by electrical or magnetic fields



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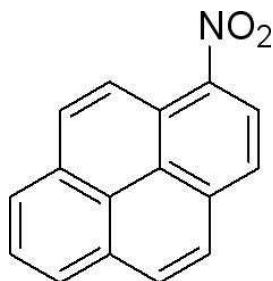
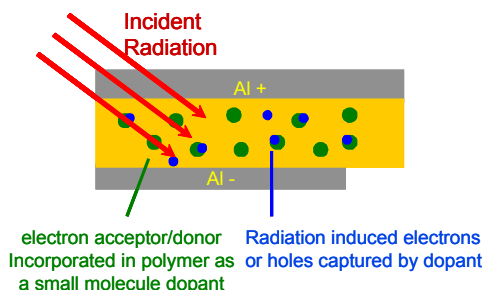


Summary & Conclusions

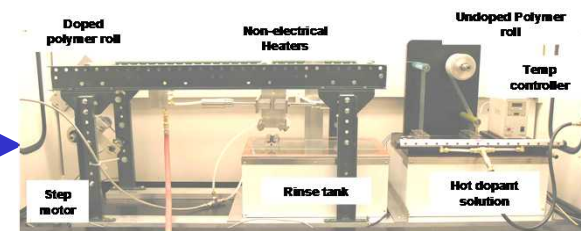
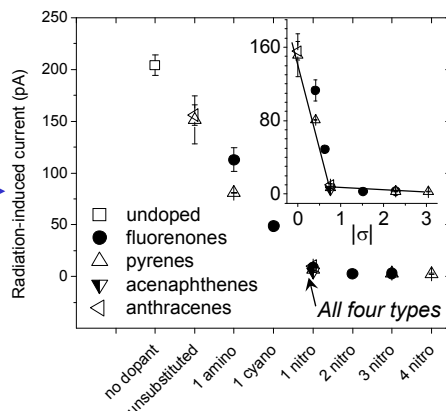
- Developed non-aqueous gels that perform over broad temperature range (polybutadiene, silicone, epoxy based gels)
 - Flexible polymer backbone
 - Low volatility solvent
 - Polymer solvent miscibility
 - Energy dissipating defects
- Entanglement screening and loop formation scaling phenomena
- Implemented gel technology in practical applications (baseline for future Sandia applications)
- Developed qualitative correlations between rheology, adhesion, and device performance that crossed material boundaries
- Pursuing solvent size effects on adhesion and adhesive aging
- Pursuing alternative gel applications



Device Functionality in Radiation Environments: Radiation Tolerant Polymer Films



Nitropyrene (NP)



Chemistry and
microstructure

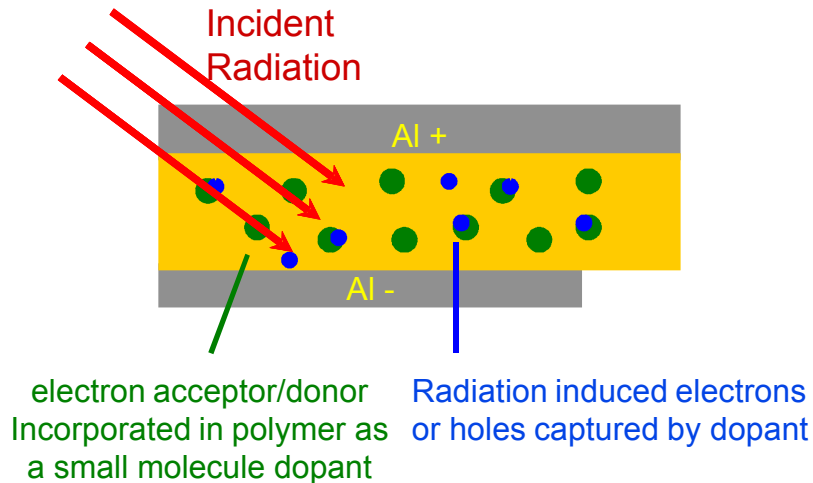
Material
properties

Process design and
implementation

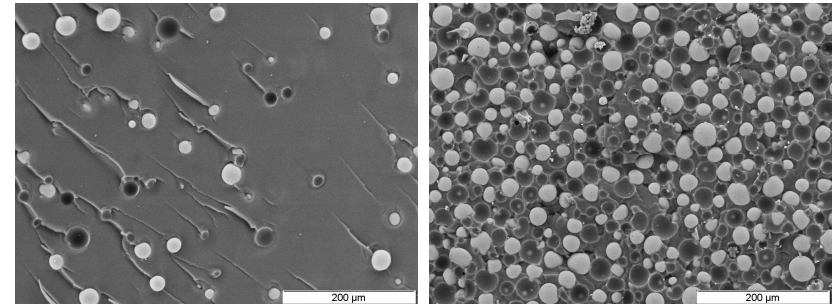


Two Approaches for Radiation Tolerant Devices

1. Engineer radiation tolerant polymers for the device



2. Develop polymeric composites to shield devices from radiation exposure



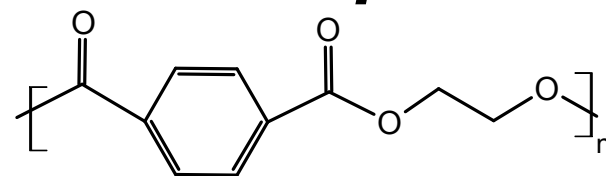
- Incorporate small molecules dopants to reduce Radiation Induced Conductivity (RIC)
- Dopants “trap” electrons or “fill” holes
- Utility for polymeric films, coatings, encapsulants, underfills, controlled conductivity coatings, sensors, etc

- High-Z particulate fillers with polymeric matrix for low density shielding composites
- Loadings from 1 to 50 volume % depending on radiation environment
- Localized “Spot” shielding of sensitive components / devices

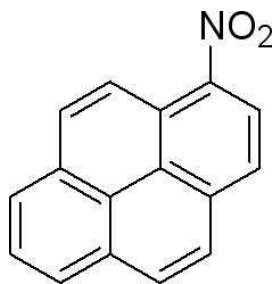
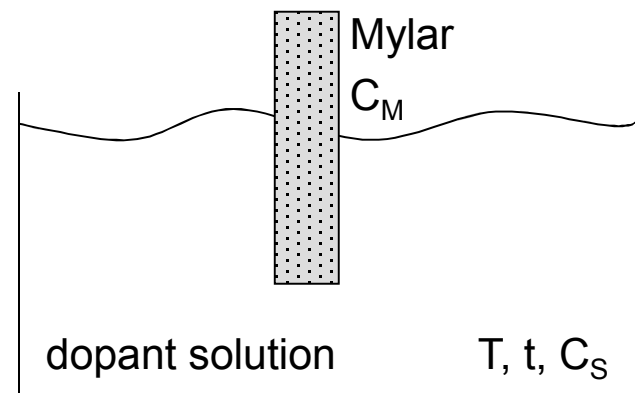


What Makes a Good Electron Trap?

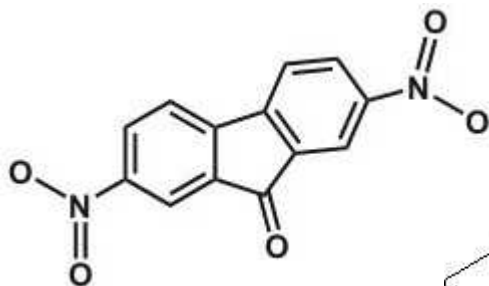
- Mobile electrons / holes generate radiation induced conductivity (RIC)
- For Mylar films electrons are more mobile
- Conjugated core with pendant electron withdrawing groups are good electron traps
- Dissolve dopant traps in warm solution and immerse polymer film (Mylar) into dopant solution
- Diffusion of dopant into polymer film



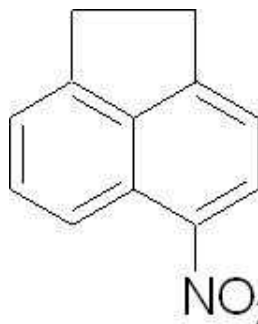
Poly(ethylene terephthalate) (PET)



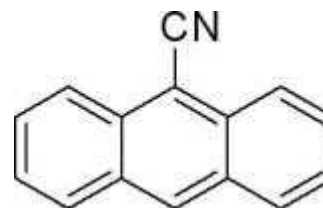
Nitropyrene
(NP)



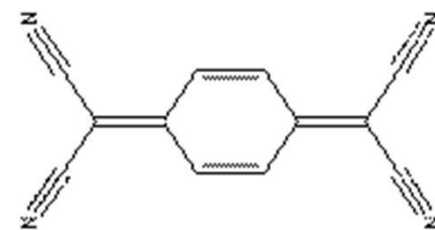
Dinitrofluorenone
(DNF)



Nitroacenaphthene
(NAN)



Cyanoanthracene
(CAN)

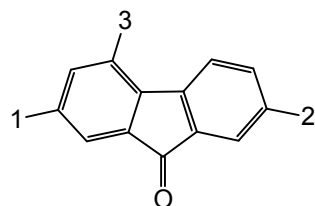
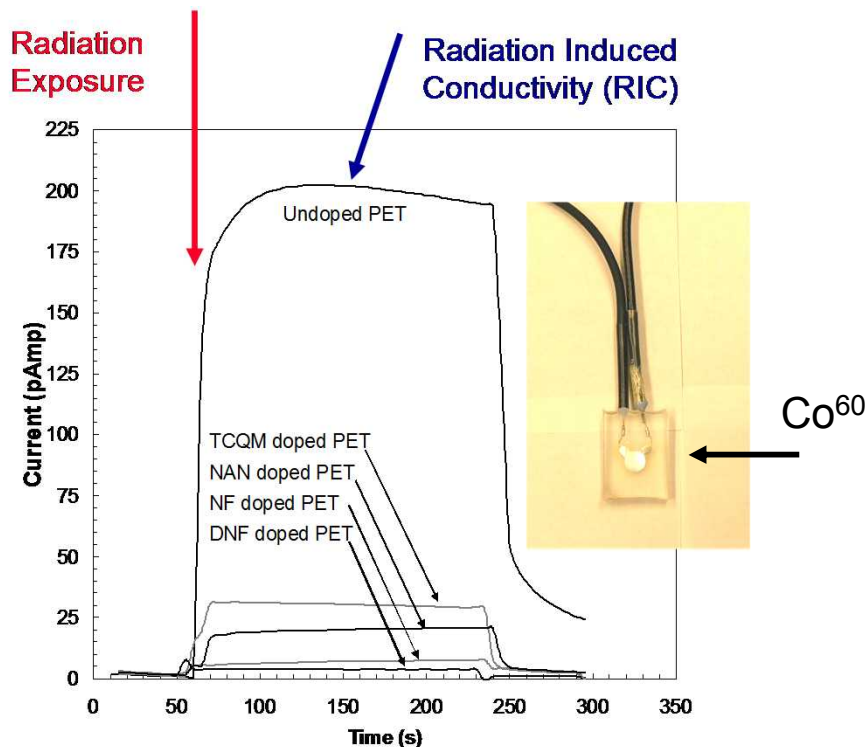


Tetracyanoquinodimethane
(TCQM)

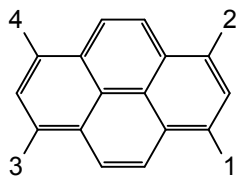
RIC Testing and Conclusions

Conclusions:

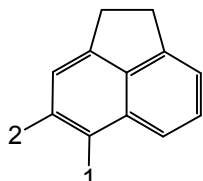
1. Aromatic core with pendant electron withdrawing groups are effective
2. Key is dopant solubility in the doping solution and in Mylar
3. Nitro withdrawing groups are most effective at RIC reduction
4. Qualitative correlation with the Hammett parameter



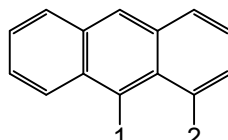
Fluorenone compounds



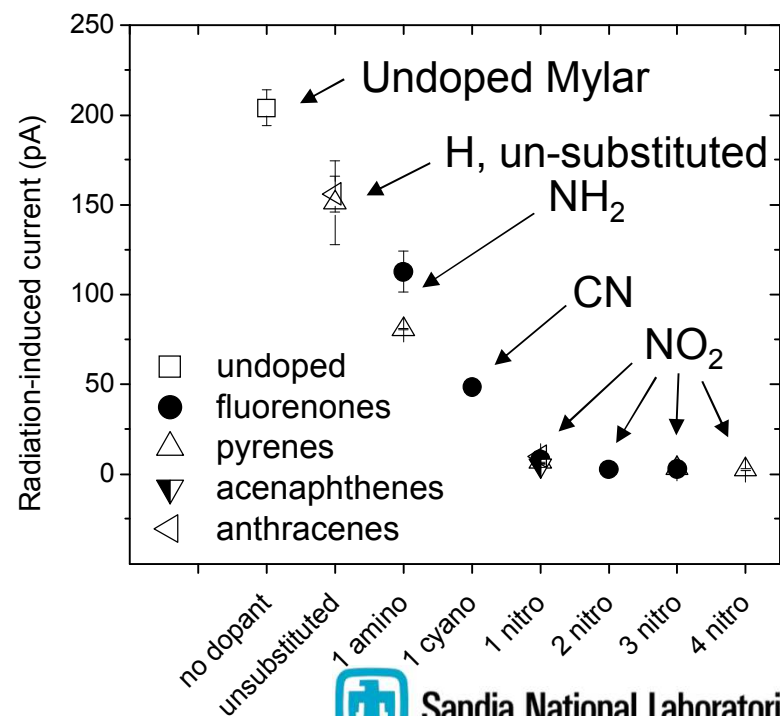
Pyrene compounds



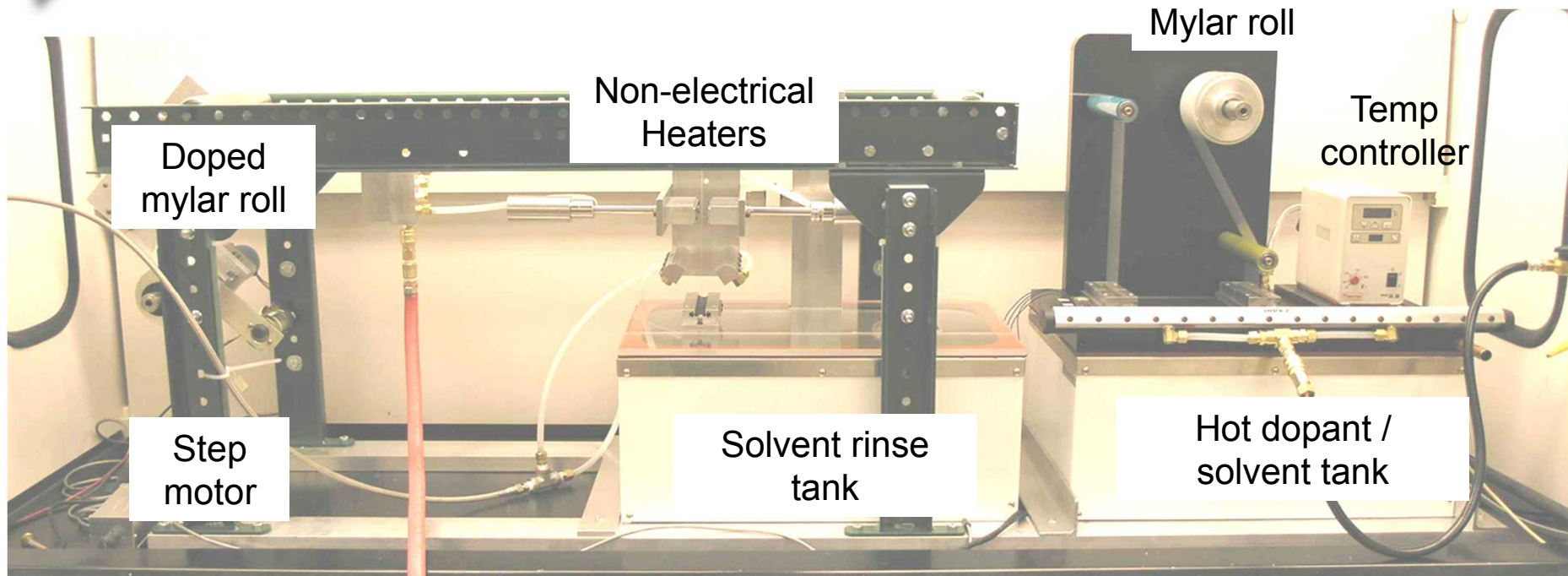
Acenaphthene compounds



Anthracene compounds



Process Development / Component Testing

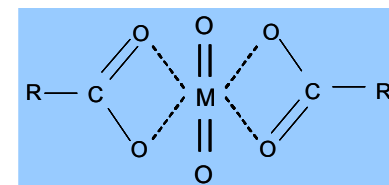


- Keys: lower-temperature and longer-time doping, IPA wash, less heaters = lower cost
- Scalable to meet future production needs
- Easily scalable to 4 ft wide Mylar rolls
- Successfully doped Mylar films with various dopants
- Excellent testing in components
- Sandia's baseline technology for future applications



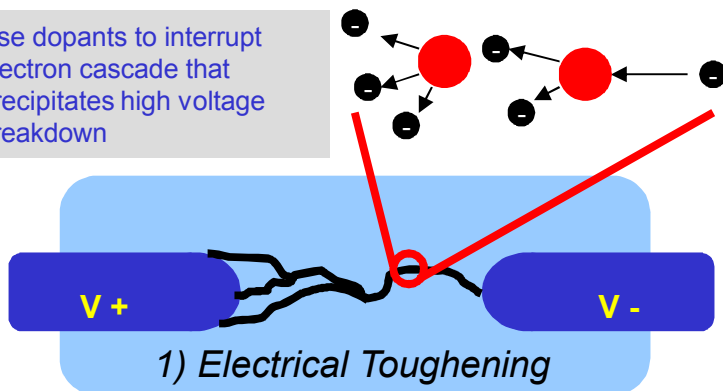
Summary & Conclusions

- Identified various small molecule electron traps that can reduce RIC in Mylar films
 - Conjugated core with pendant electron withdrawing groups
 - Qualitative correlation with Hammett Parameter
- Adsorption / diffusion process controls dopant uptake in film
 - Langmuir adsorption
 - Fickian Diffusion
- Designed pilot-scale process for doping Mylar films
 - Processed 100's of feet with various dopants
 - Excellent testing in real components
 - Scale-up in FY09
- This technology is now the “baseline” at Sandia
- Future: materials / process optimization and alternative applications



3) *Sensors*

Use dopants to interrupt electron cascade that precipitates high voltage breakdown

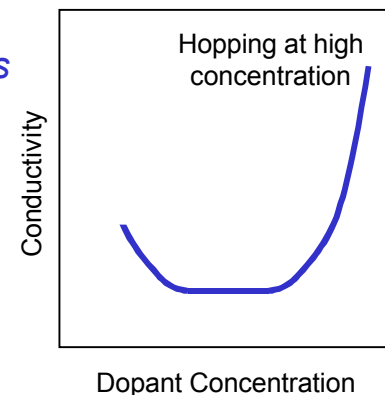


2) *Potential alternative applications for doped polymers*

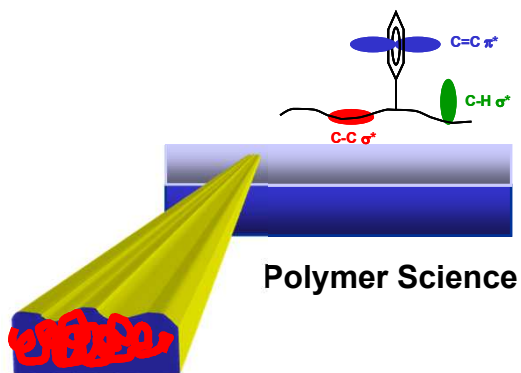
- Molecular / organic electronics
- Anti-static coatings
- Conductive / non-conductive filler coatings
- Nano-wires / conductive fibers



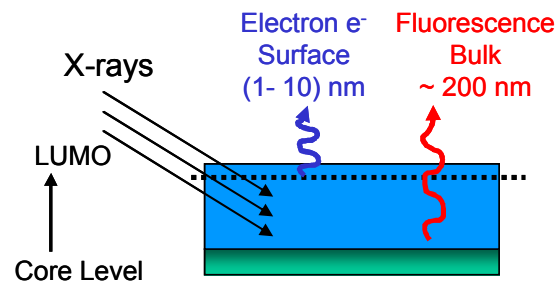
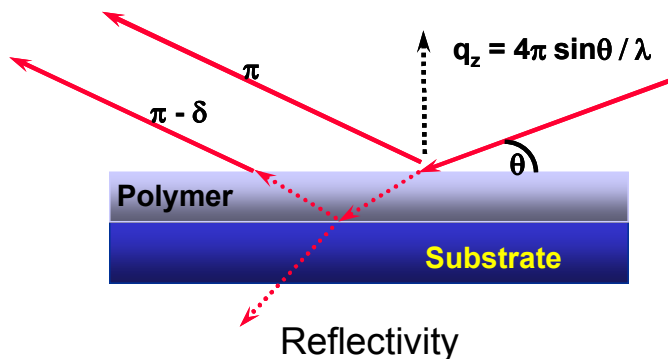
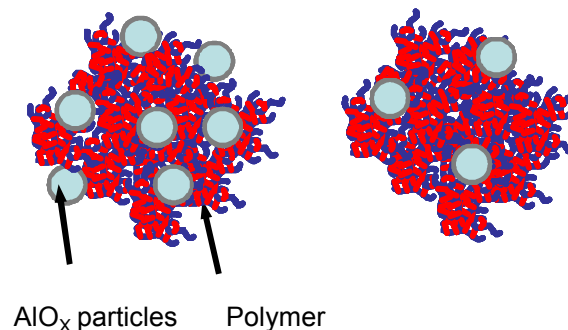
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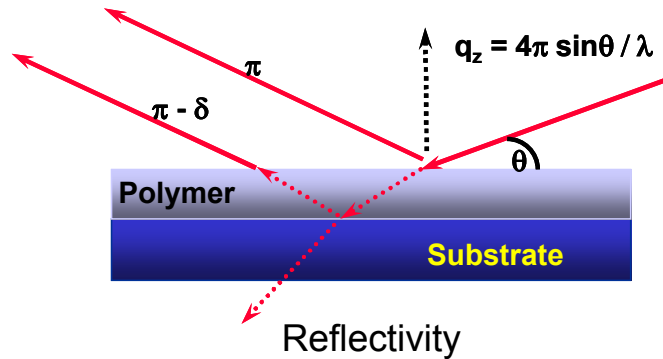
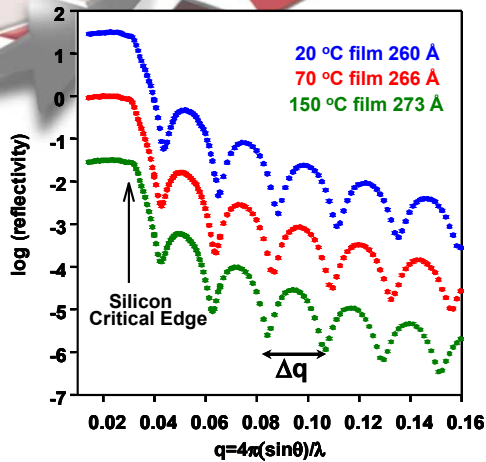
Other Programs: Thin Films and Interfaces, Polymer Composites, Synchrotron Based Interfacial Science



Polymer Science

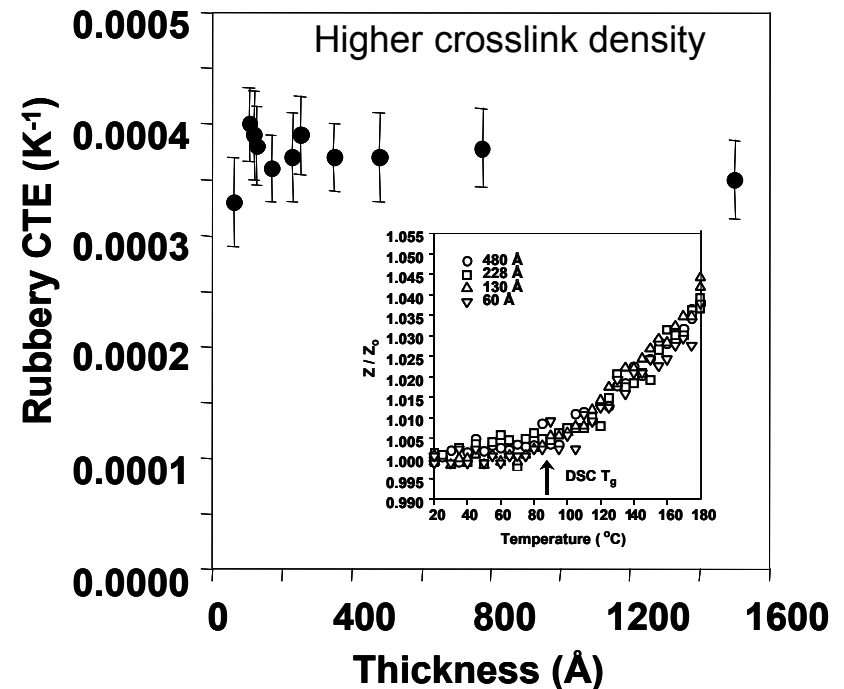
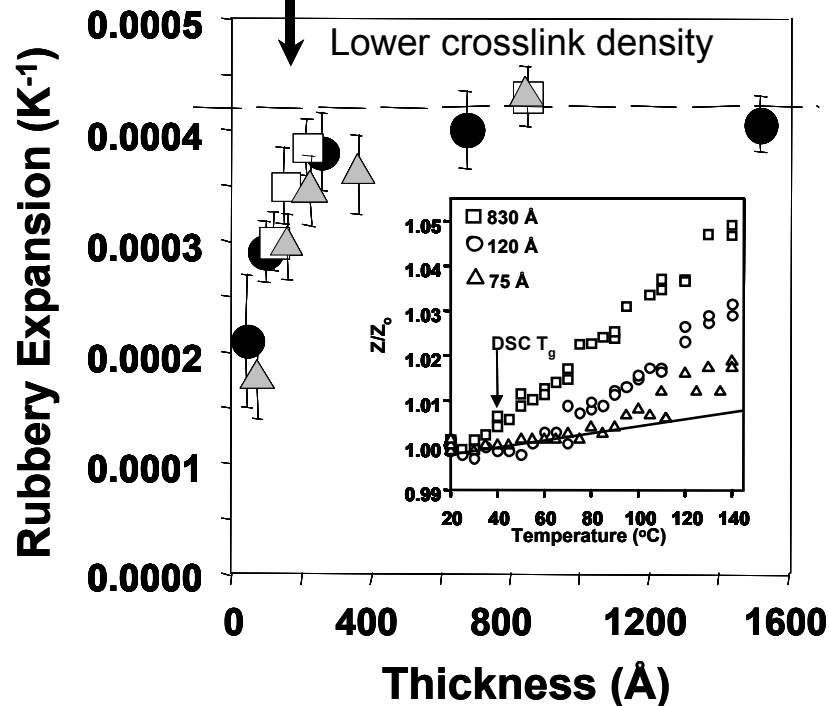


Polymer Thin Films and Interfaces



- X-ray reflectivity to accurately measure thickness of thin films
- Loosely crosslinked ($T_g \sim 40^\circ\text{C}$) films exhibited glassy expansion well above bulk T_g and decrease in rubbery CTE with film thickness
- Changes in thermal properties were independent of surface treatment
- Highly crosslinked films ($T_g \sim 90^\circ\text{C}$) did not exhibit a change in thermal properties

$$t = 2\pi / \Delta q \quad 10 \text{ crosslinks}$$



Synchrotron Based Interfacial Science

Expanding Beamline Capabilities

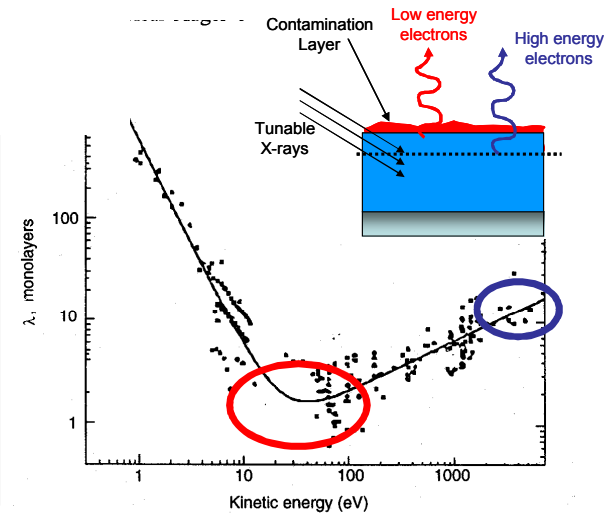
a) Low energy beamline (180 to 1200 eV)

- Low Z elements (C, N, O, F)
- organic films and metal oxides

b) Mid energy beamline (1000-8000 eV)

- recently refurbished
- NEXAFS
- High energy XPS

c) High energy beamline (7 to 30kV)



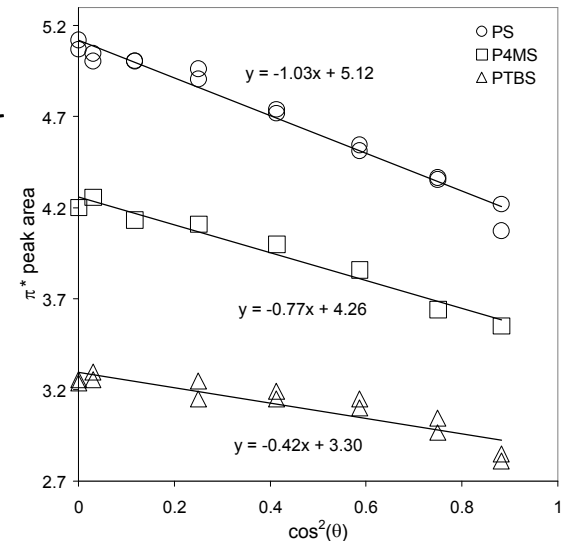
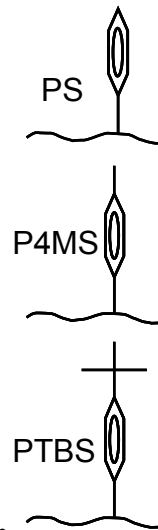
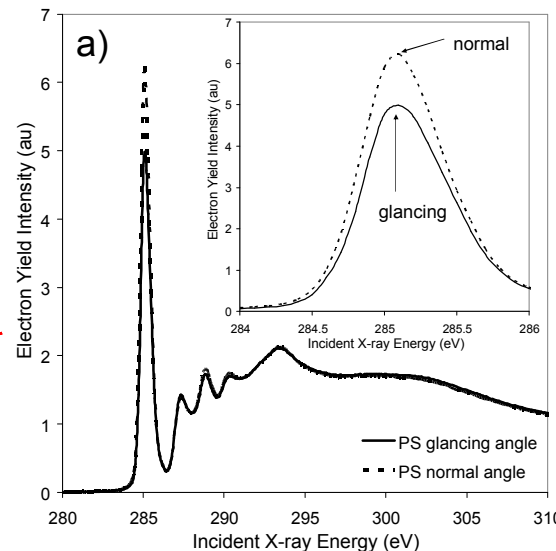
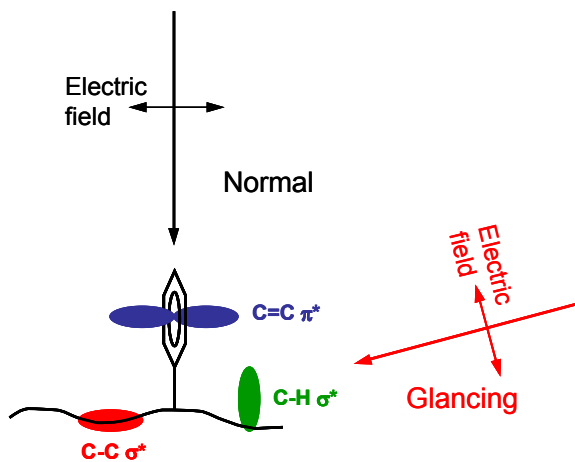
M.P. Shea, W.A. Dench, *Surf. Interface Anal.*, 1, 2 (1979).

Synchrotron Advantages

- High intensity
- Monochromatic
- Tunable
- Polarized

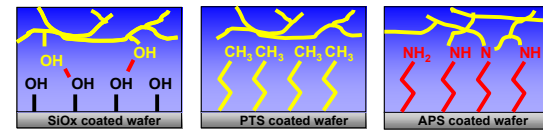
New Measurement Development: Enhanced Depth Profiling Analysis for Composition Gradients and Buried Interfaces

1. Variable voltage bias on electron yield detector
2. Analysis of Auger energy loss with XPS
3. High energy XPS exploiting "universal curve"



Polymer Composites

1. Encapsulants



4) Filler surface chemistry

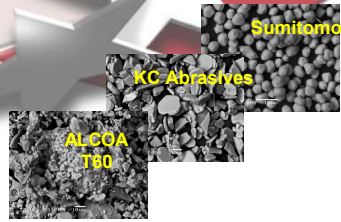
Future

- Sub-micron and nano-particle loadings
- Surface treatments / microstructure
- Tunable coatings

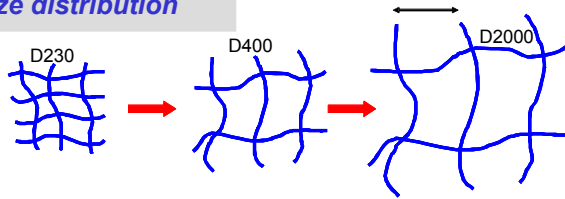
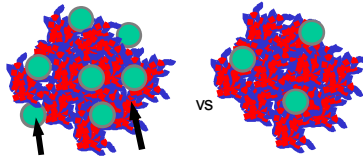
Conclusions

- Alumina-epoxy composites are robust
- Variable changes have minimal impact on cured properties
- Viscosity is sensitive to shape / size / distribution / loading
- Relax materials specifications
- Processing is key

1) Particle shape, size, and size distribution



2) Filler loading

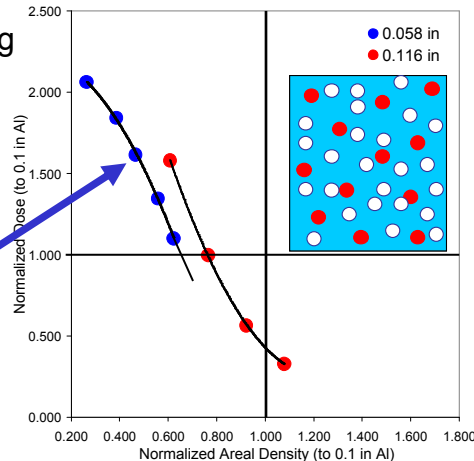


3) Polymer crosslink density

2. Radiation Shielding

High-Z filled conformal coating

Electronic Device



Results / Goals

- 35% mass reduction
- > 50% mass reduction

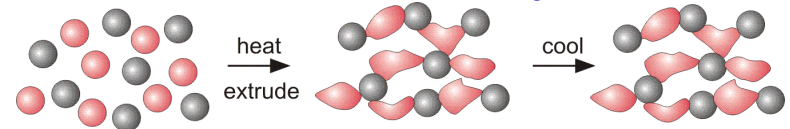
Challenges

- Particle settling (conductivity)
- Transparency in thin films

Solutions

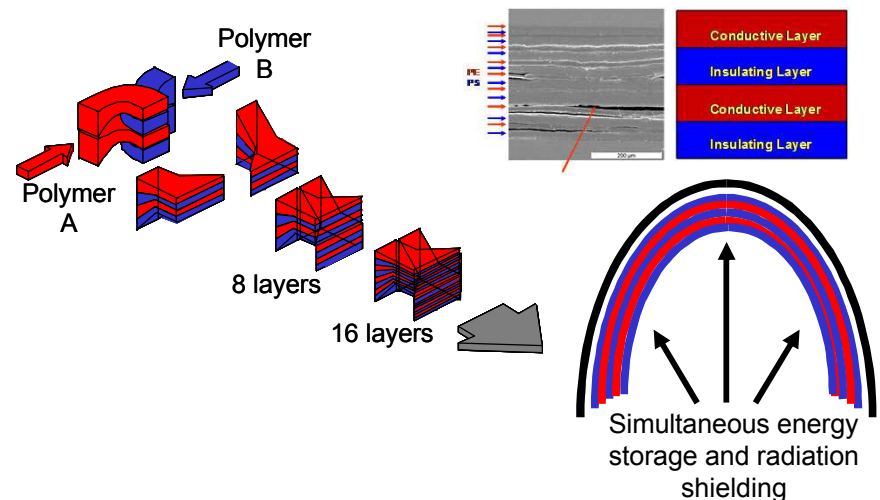
- Sub-micron / nano-particles
- Insulating surface coatings
- Low density fillers
- Localized or global

3. Conductivity



Results

- Solid filler with low melting filler (10 μm to 100 nm)
- Conductivity consistent with percolation (1-10 $\Omega\cdot\text{cm}$)
- Processable viscosity
- Sub-micron and nano-particles for future applications





Acknowledgements

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Additional Gel Contributors: Lori Arthur (Dow Corning), Bob Baron, Mark Braithwaite, Bob Brooks, Beth Brown, Scott Campin, Myrriah Chavez, Jennifer Corona, John Emerson, Jim Harris, Ronald Hedden (Penn State University), Tina Huber, Patrick Klein, Adam Lester, Chau-Jean Lin (Northwestern Univ.), Ann Norris (Dow Corning), Guy Prevost, Kanamu Pupuhi, Charles Retallack, Chris Rondeau, Gayle Schwartz, Ken Shull (Northwestern Univ.), Cathy Sobczak, Burcu Unal (Penn State University), Bob Winters, and Sean Winters.

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Synchrotron: Daniel Fischer

External Collaborations: Daniel Fischer (NIST, synchrotron), Ronald Hedden (Penn State, scattering), Richard Parnas (UCONN, composites), Ken Shull (Northwestern, soft materials), Bret Chisolm (North Dakota State University, combinatorial research on porous materials)