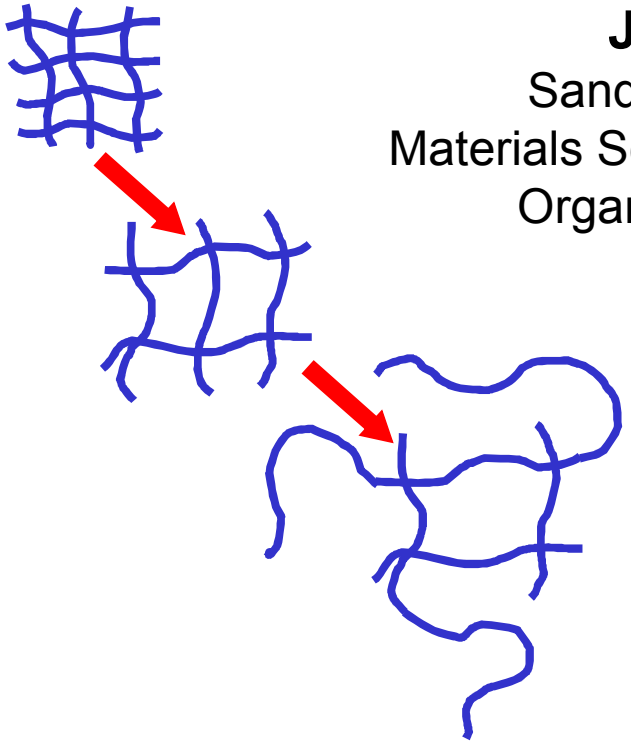
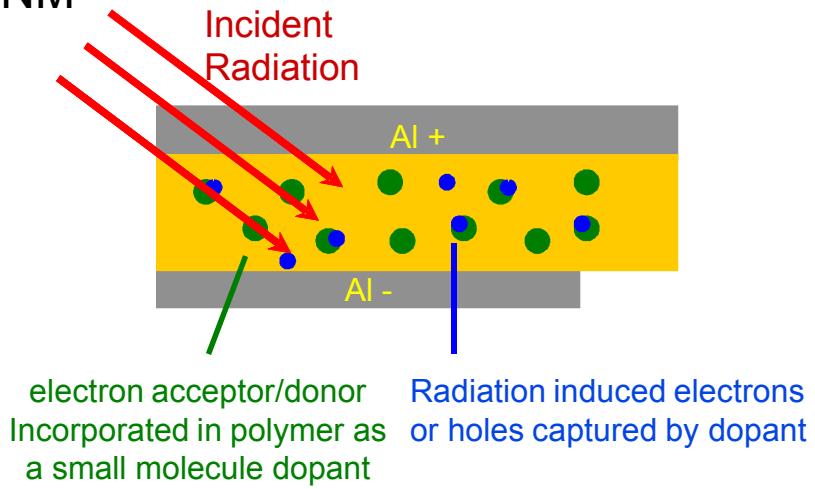
SAND2008-0845P

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



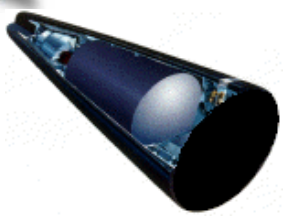
1. Non-aqueous polymer gels



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 Safety Administration under contract DE-AC04-94AL85000.

Sandia Mission Areas



1) Nuclear Weapons

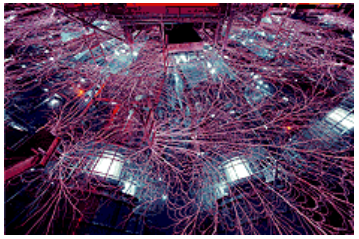
- Weapons surveillance
- New technology
- Maintain safe, secure, reliable stockpile
- Update weapons

Nuclear Weapons Complex

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

2) Non-proliferation

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



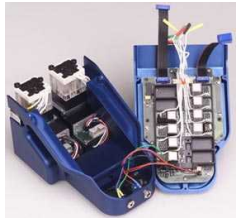
Science, Technology, Engineering

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

National Security Laboratory

Defense Systems and Assessment

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



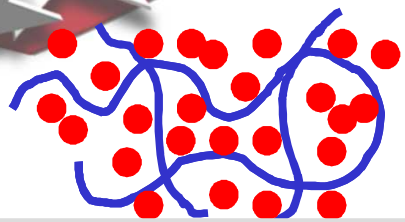
Homeland Security and Defense

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

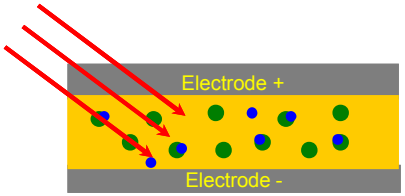
Energy and Infrastructure Assurance

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

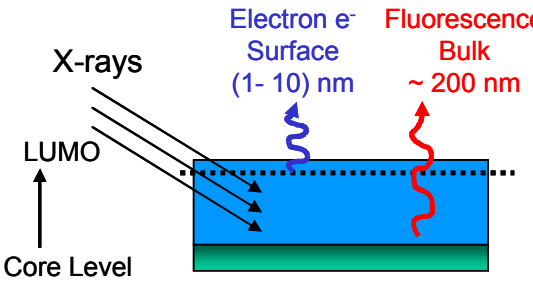
Various Projects



1) Soft Polymers / Gels / Elastomers

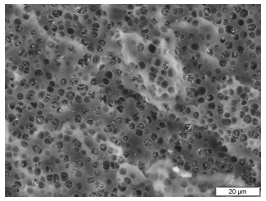


2) Radiation Tolerant Organic Materials

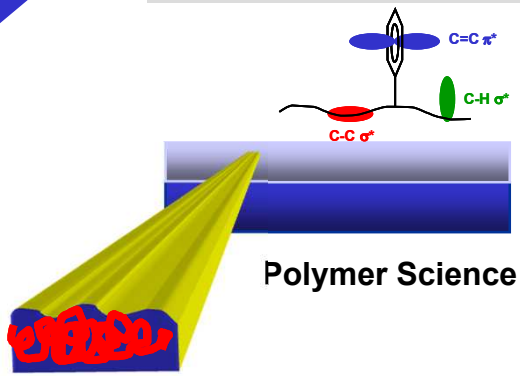


3) Thin organic films / interfacial characterization

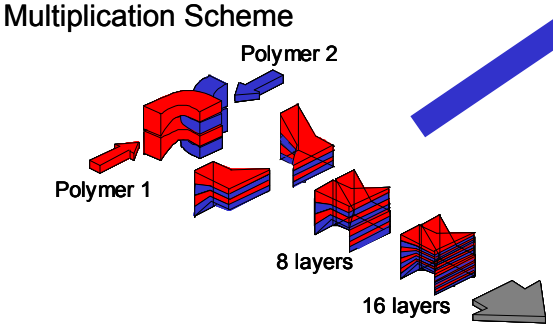
7) Polymeric materials for sensors



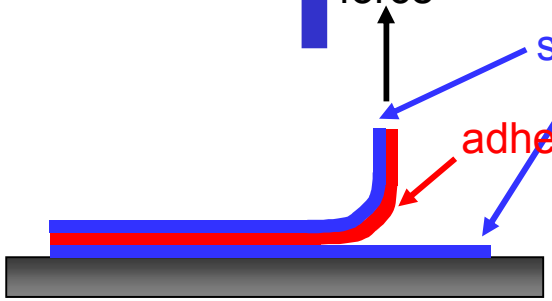
1. Interfacial science
2. Large budget ($2-3M/yr)
3. Large team (staff, postdocs, technicians, students, external collaboration)



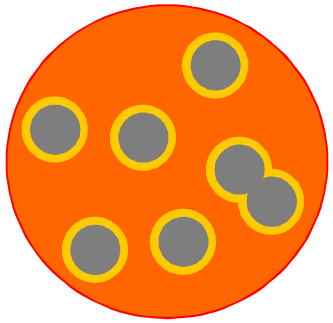
Polymer Science



6) Multilayer Coextrusion



5) Polymer adhesion / adhesive and polymeric degradation

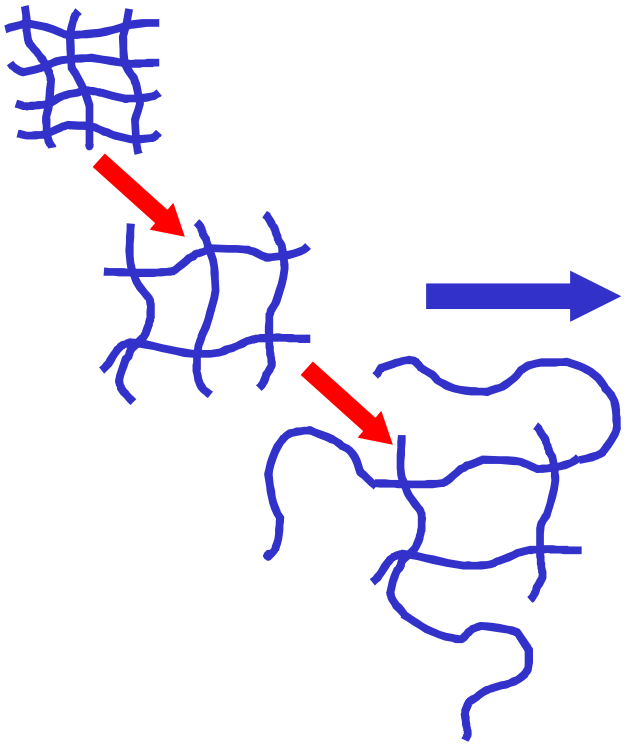


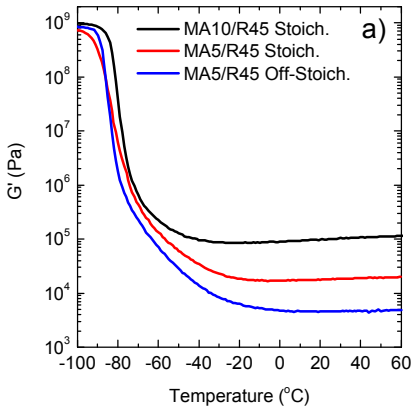
4) Polymer Composites / Nanocomposites

Joseph L. Lenhart (1821)

Sandia National Laboratories

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



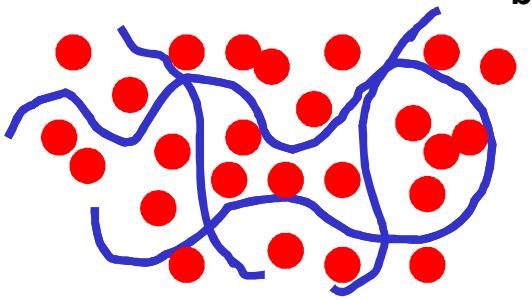


Chemistry and microstructure → Material performance → Process design and implementation

Gel Technology Can Enable Various Applications

Tunability offers applications

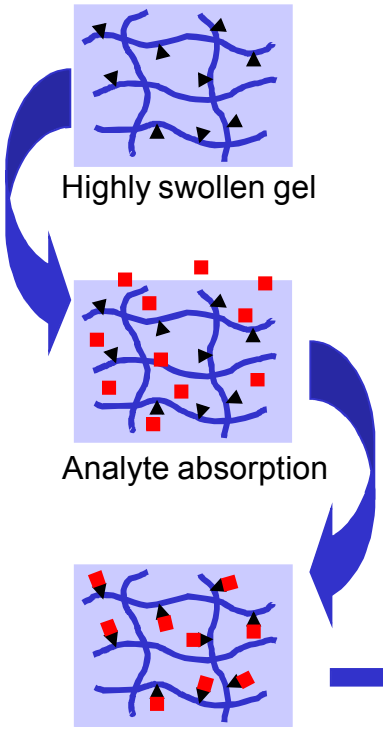
- Polymer chemistry
- Solvent loading
- Solvent type
- Fillers / additives



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

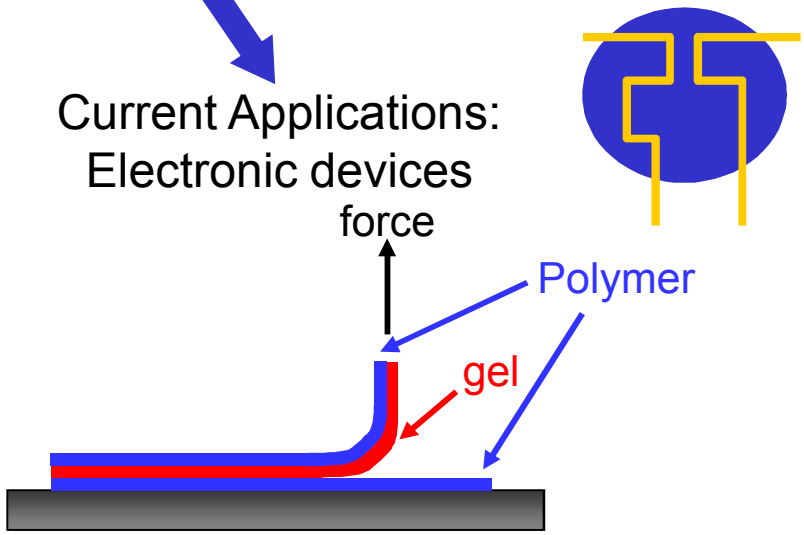
- Flexible backbone
- Low volatility solvent
- No polymer or solvent transitions
- Polymer – solvent miscibility
- Good adhesion to a variety of substrates without surface preparation
- Adjustable reaction rate for various applications

Impact



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

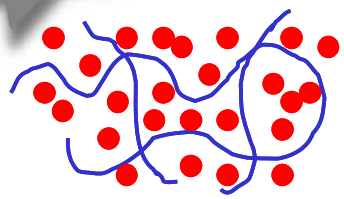
Current Applications: Electronic devices



Gel – substrate adhesion is critical for device performance

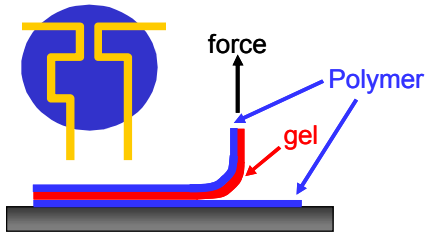
Sandia National Laboratories

Various Gel Chemistries Offer Promise

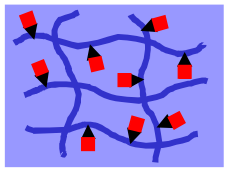


Challenges:

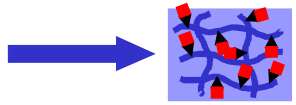
1. Broad temperature performance
2. Long lifetime



Electronics Encapsulation



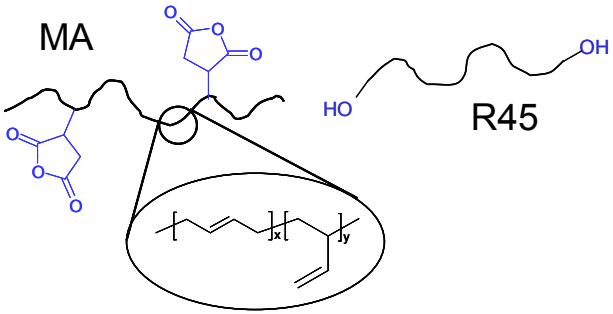
Analyte-receptor bonding

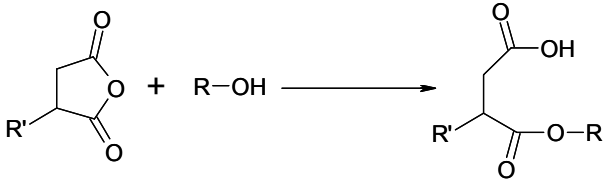


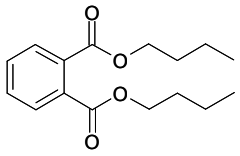
Gel shrinkage And detection

Sensors

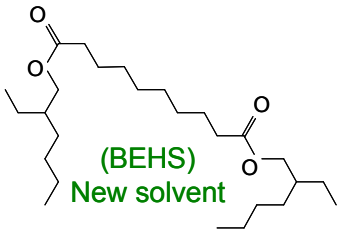
Polybutadiene





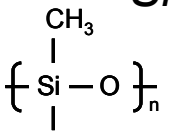


(DBP) old solvent

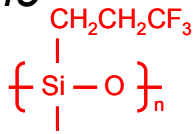


(BEHS) New solvent

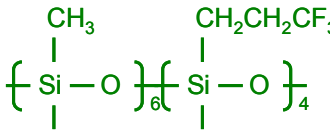
Silicone



DC 3-6635

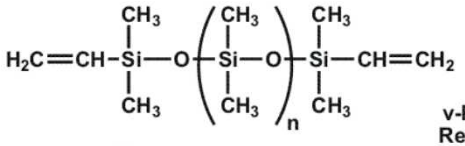


DC 4-8022

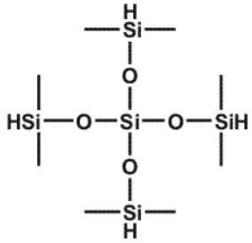


Commercial materials

EG 1000

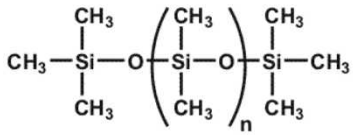


v-PDMS
Reactive
Vinyl Terminated PDMS



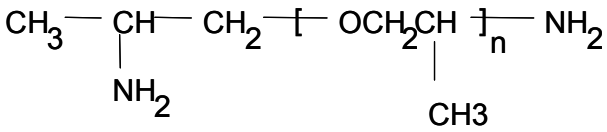
Tetrafunctional Silane Crosslinker

Model System

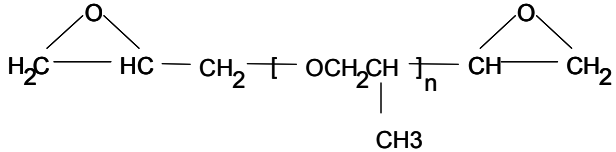


m-PDMS
Non-reactive
Methyl Terminated PDMS

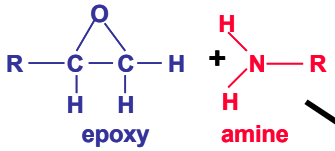
Epoxy

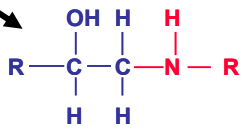


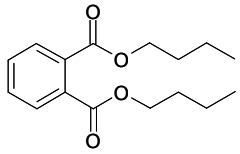
4000, 2000, 400, 230 g / mole



PPGDE 640, 380 g / mole







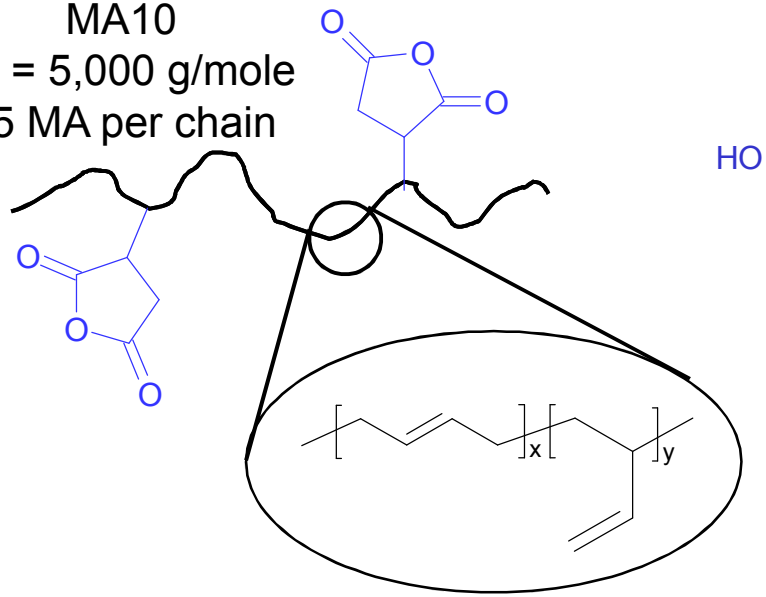
(DBP)

Sandia National Laboratories

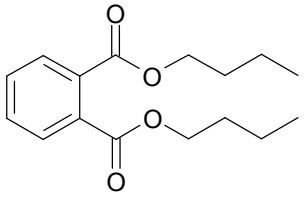
Initial Gel Formulation (MA10 Gel)

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)

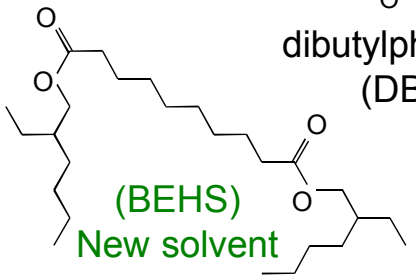
MA10
M_n = 5,000 g/mole
~5 MA per chain



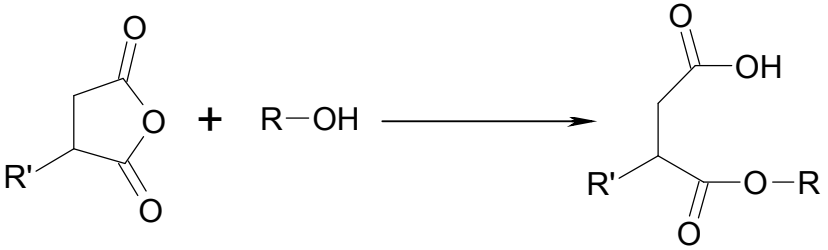
R45
M_n = 2,500 g/mole
~2.5 OH per chain



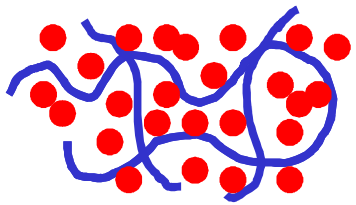
dibutylphthalate
(DBP)



crosslinked polybutadiene matrix surrounding the solvent.



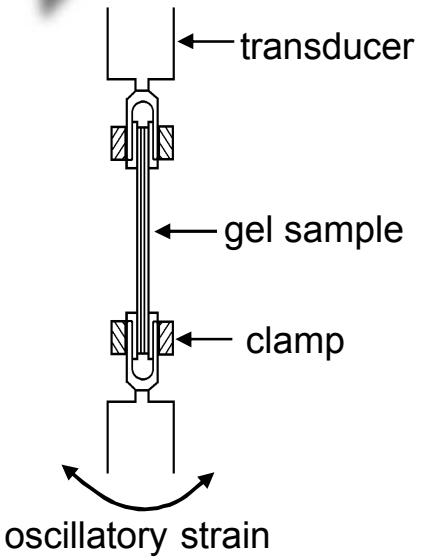
crosslinking reaction



Crosslinking Reaction (promoted with tertiary amine catalyst)

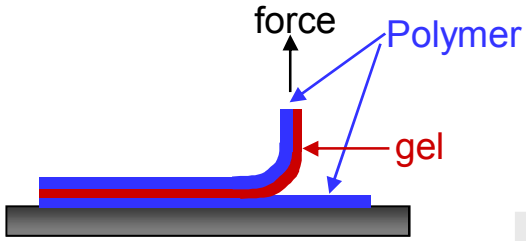
Sandia National Laboratories

Analysis Tools



Rheology

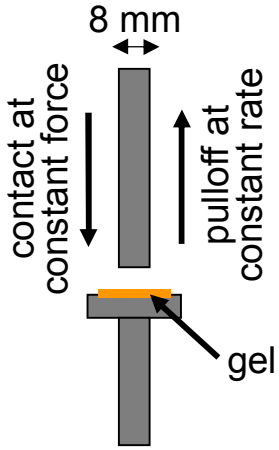
- Measure modulus / "stiffness" from -100 °C to 70 °C
- Look for changes in behavior



90° Peel

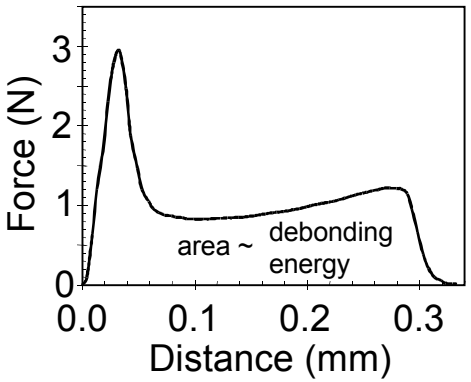
- Evaluate strength of gel - Polymer interface
- Low peel rates minimize energy dissipation

$G = G_o + G_o[f(\text{peel rate}, T)]$

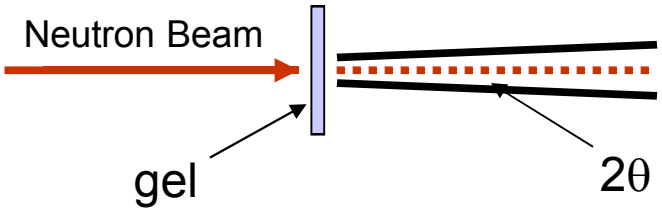


Tack

- Evaluate "stickiness"



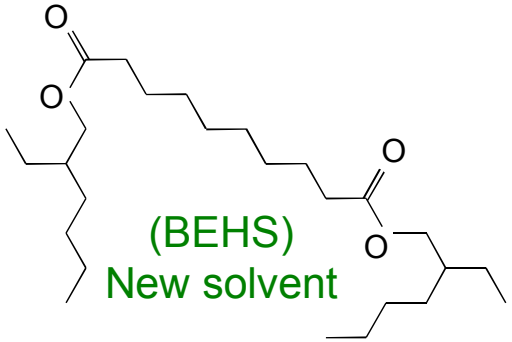
Neutron Scattering

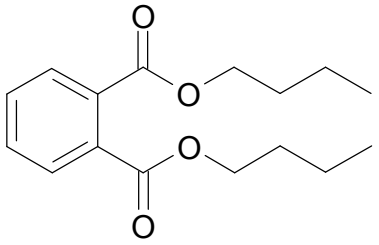


- Evaluate phase behavior

Choosing Alternative Solvents

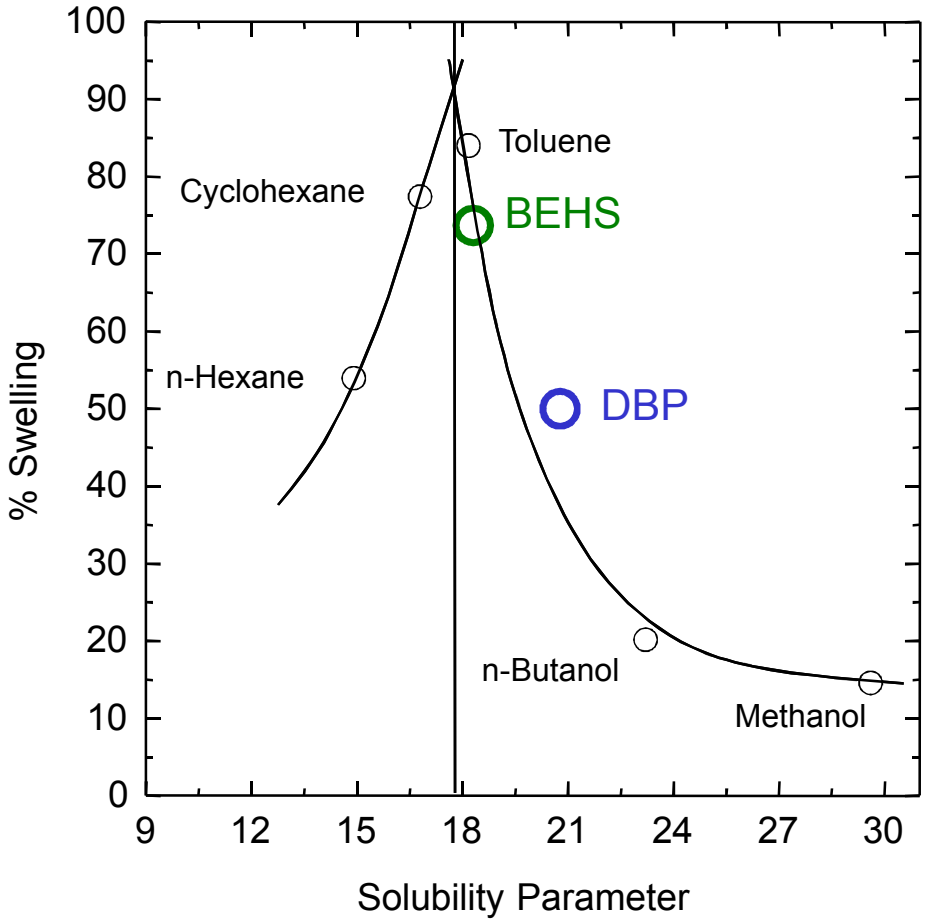
Polymer swelling experiments immerse crosslinked polybutadiene in solvents with different solubility parameters



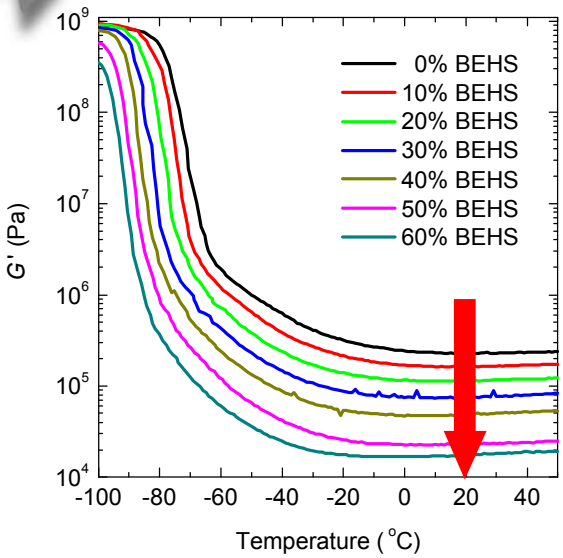


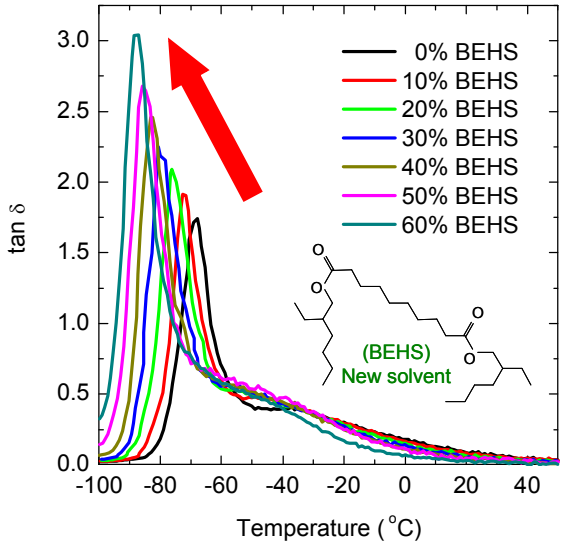
- Maximum in swelling corresponds to average network solubility parameter
- $\chi \sim (\delta_{solvent} - \delta_{polymer})^2$
- Highest miscibility when $\delta_{solvent}$ equals $\delta_{polymer}$

- BEHS shows promise for broad temperature performance gels. Other solvents are too volatile



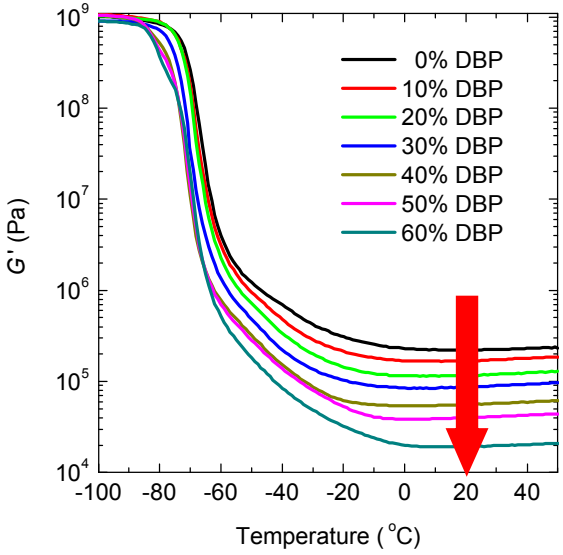
Solvent Impact on Mechanical Properties

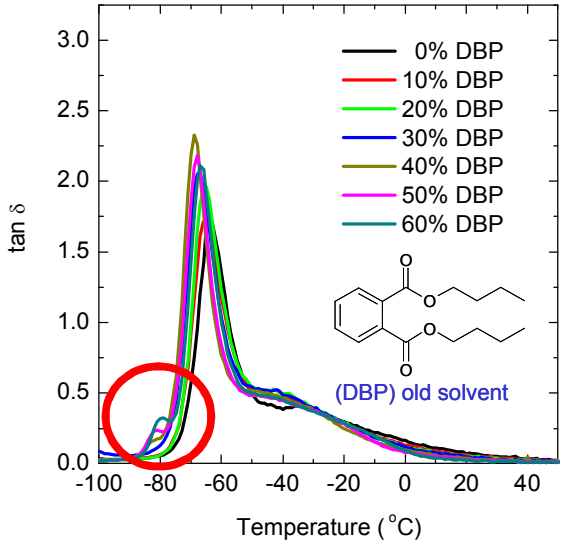




- Plateau modulus at T > -40 °C
- Increase in solvent content suppresses modulus and T_g

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

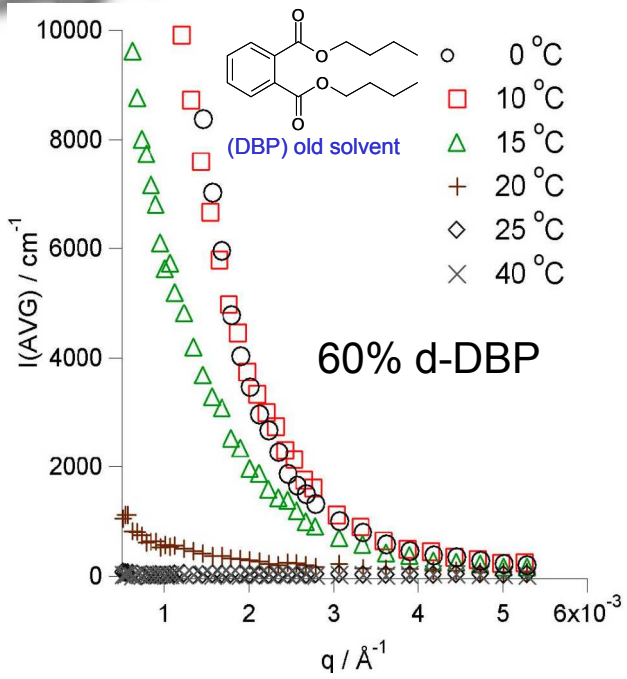


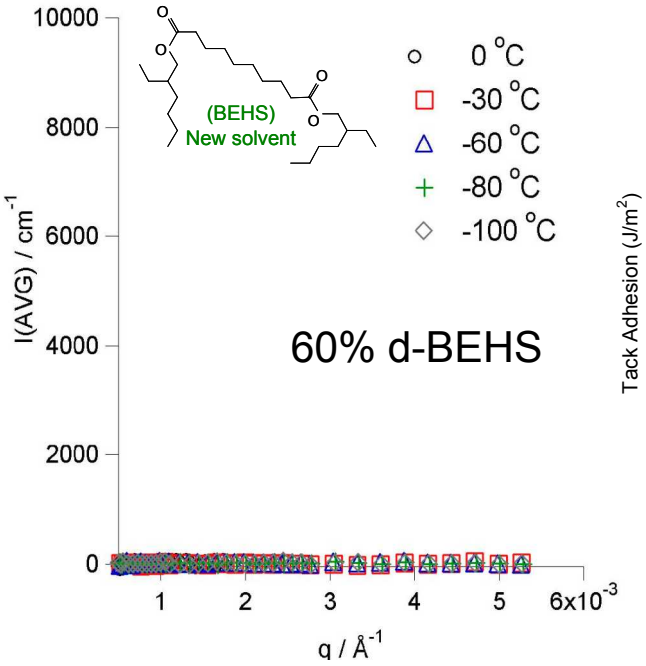


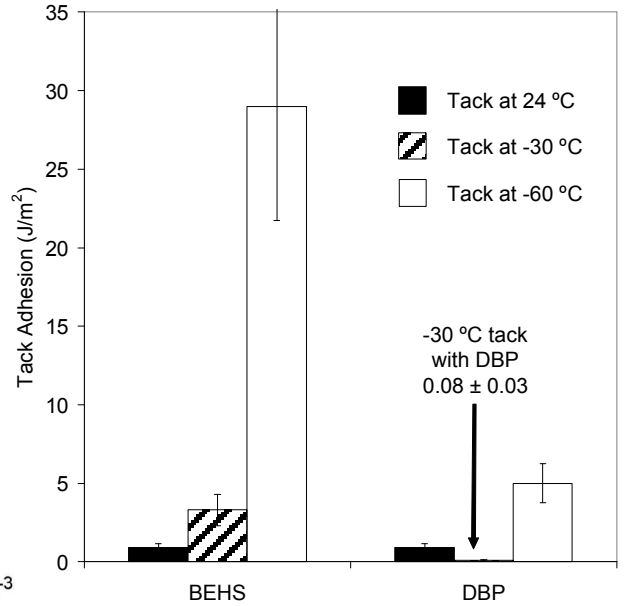
- Plateau modulus at T > -10 °C
- Modulus suppression with increasing solvent
- Phase separation with increasing solvent

Neutron Scattering

Prof. Ronald Hedden
Penn State Univ.
Materials Science Dept





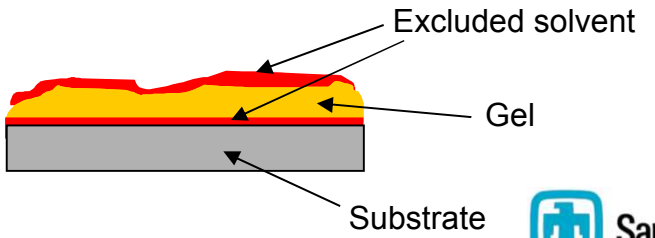


- Strong scattering temperature dependence
- 60% DBP phase separates below 20 °C
- 80% DBP phase separates below 60 °C

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

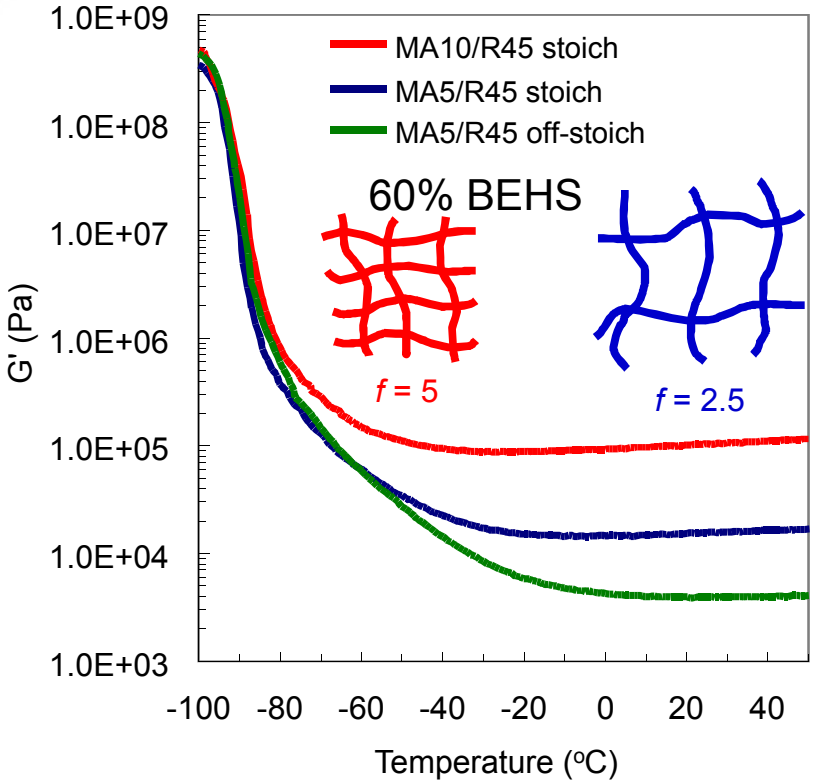
- Tack adhesion degrades with phase separation
- Devices fail due to gel delamination at critical interfaces

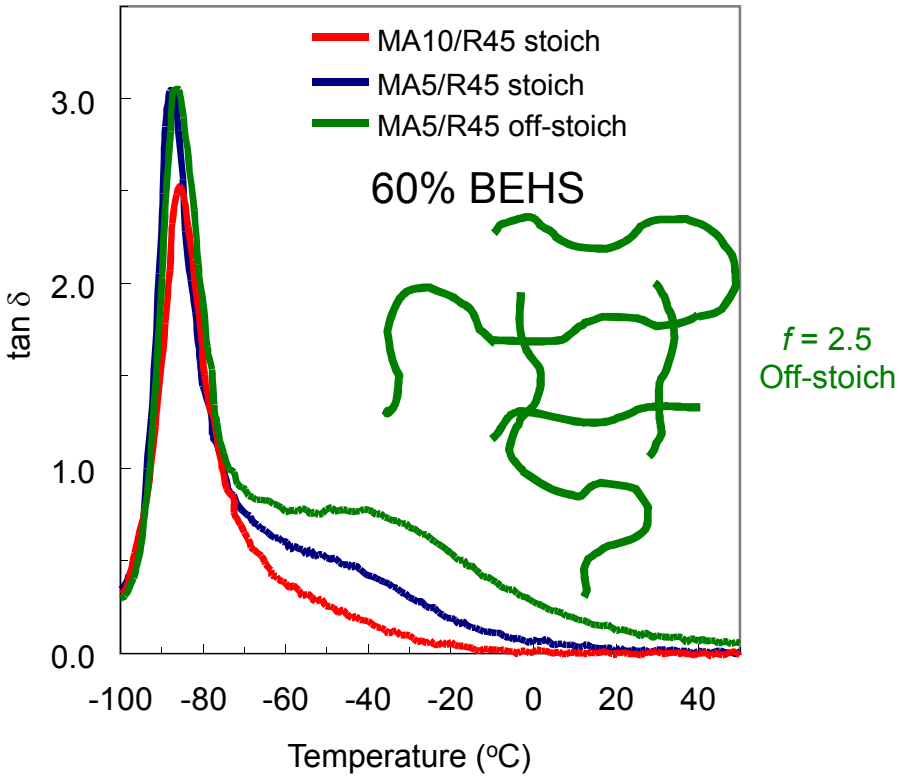
Switching to a solvent miscible over the device operating temperature range resulted in dramatic improvements in device performance



Sandia National Laboratories

Impact of Cross-link Density



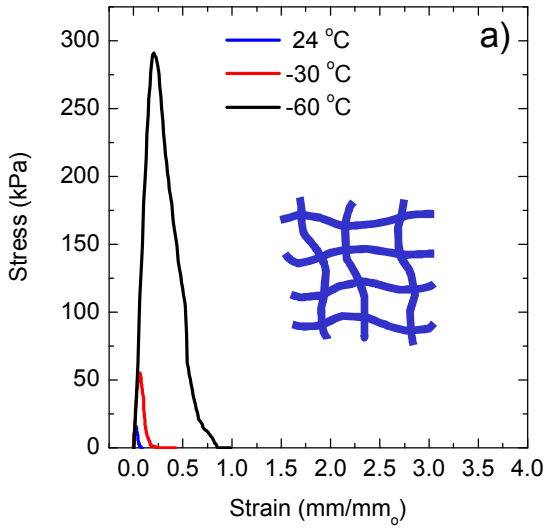


- Decreasing crosslink density decreases plateau value (reduced functionality, offstoichiometry)
- T_g identical
- Extractables equal at 61.5 ± 0.5%

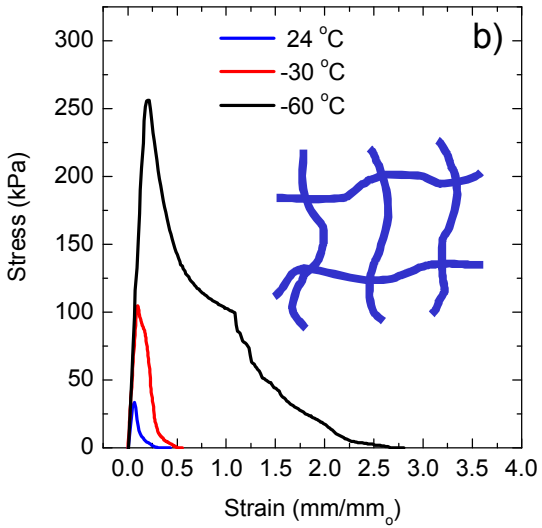
- Similar loss tangent behavior
- Increase in loss tangent (0 to -70 °C) with decreasing crosslink density
- Defects in the gel structure? ie. dangling ends

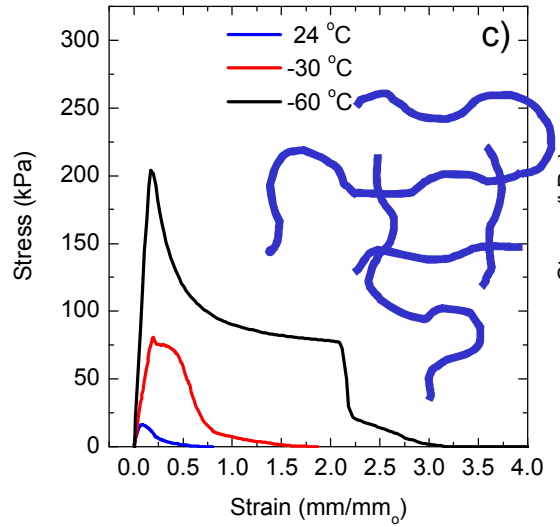
Correlation with Stress-Strain Diagrams

MA10 stoichiometric

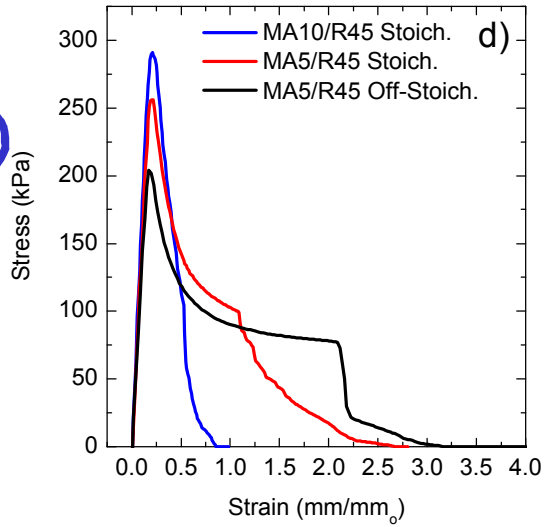


MA5 stoichiometric

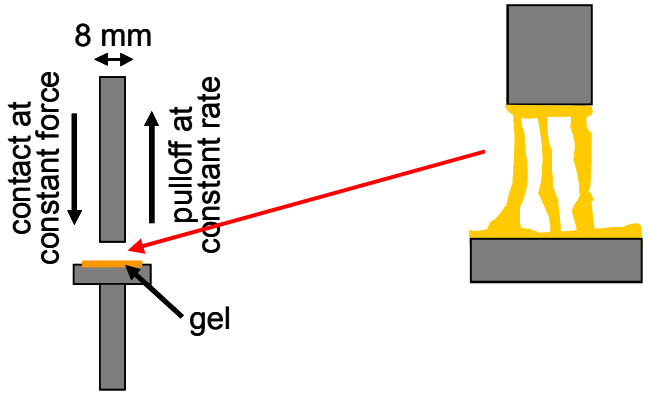




MA5 off-stoichiometric



Comparison at -60 °C

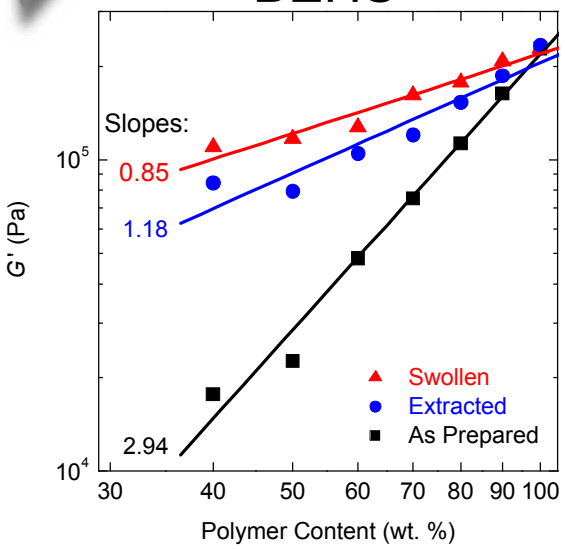


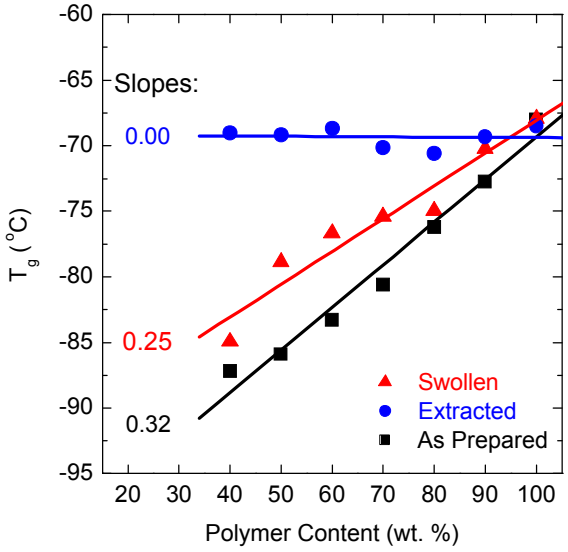
- As temperature decreases maximum and area increase (consistent with increasing loss tangent)
- As crosslink density decreases extension increases at all temperatures
- MA10 gels fail elastically even at low temperatures (small loss tangents)
- MA5 gels exhibit extension and fibrillation (high loss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

Sandia National Laboratories

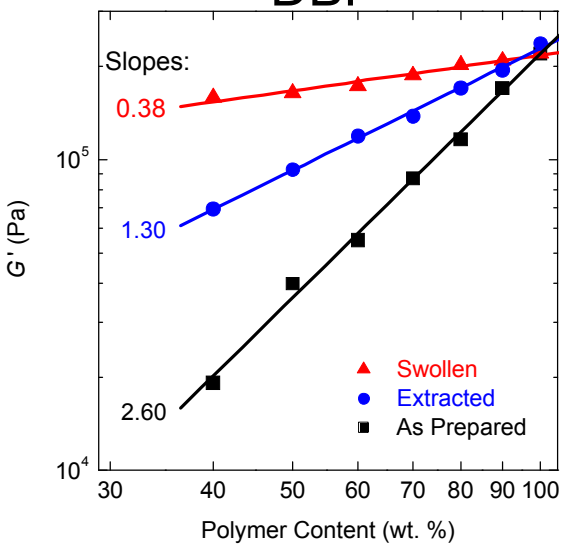
Processing Impact on Effective Crosslink Density

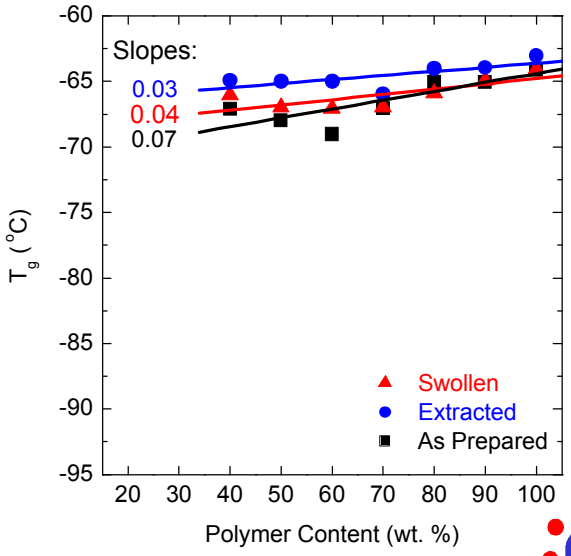
BEHS





DBP

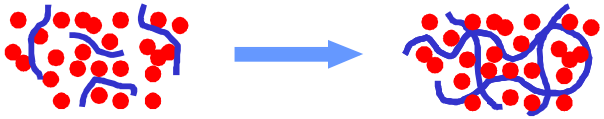




1. Different processing approaches required for various applications
2. As solvent loading increases in "as prepared" gels the entanglement density decreases
3. Processing (micro-structure) has bigger impact on properties than solvent loading
4. Entanglements do not impact elastomer Tg

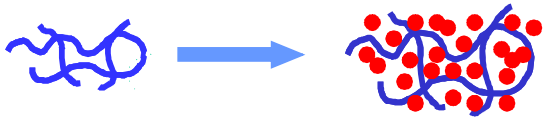
Black – "As Prepared"

Mix polymer and solvent and cure together



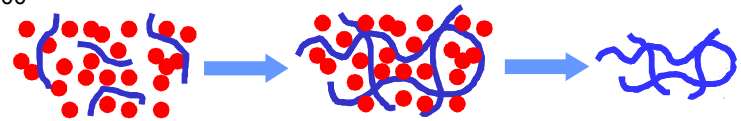
Red – "Swollen"

Cure polymer without solvent and swell to the desired solvent loading

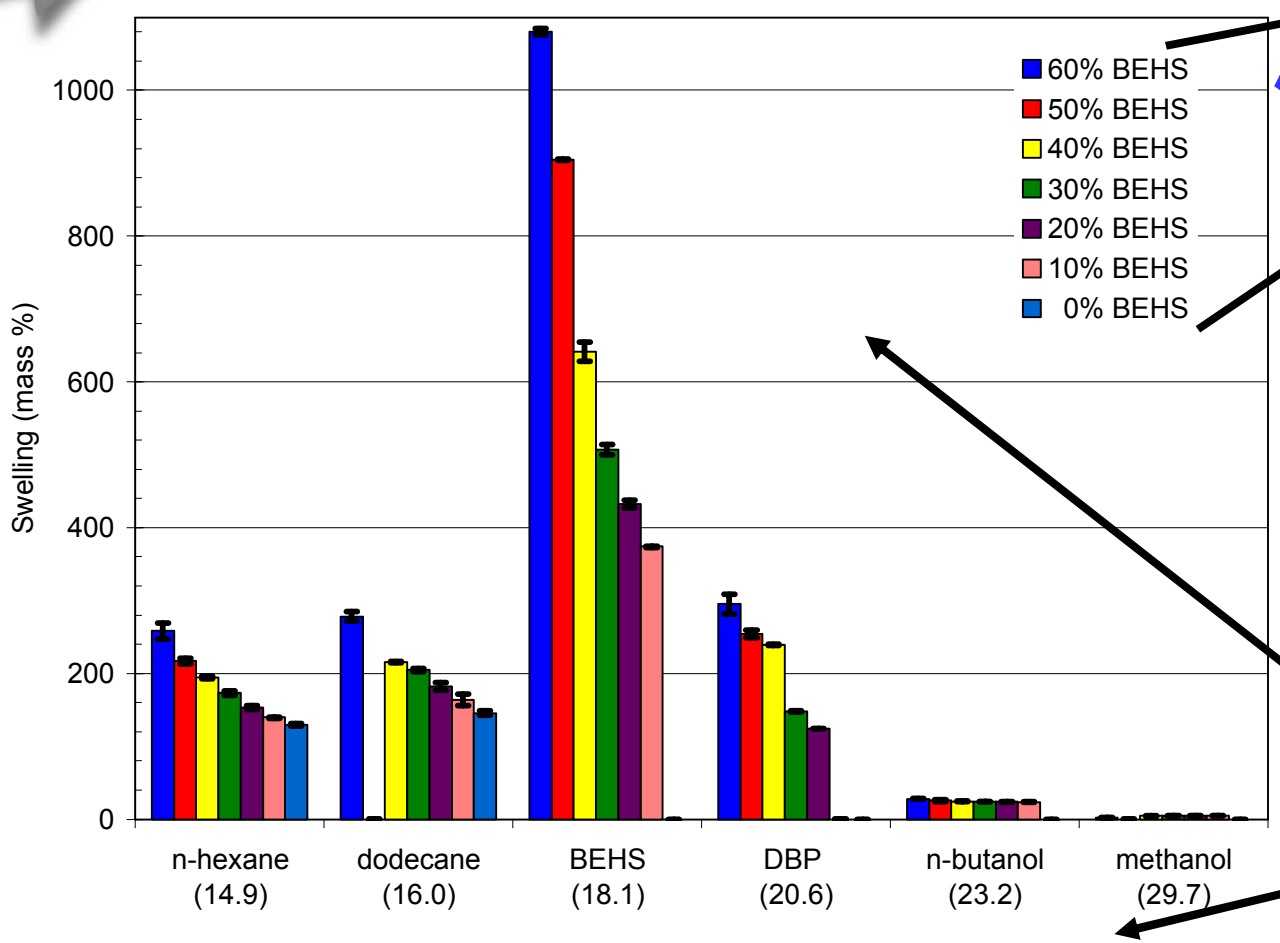


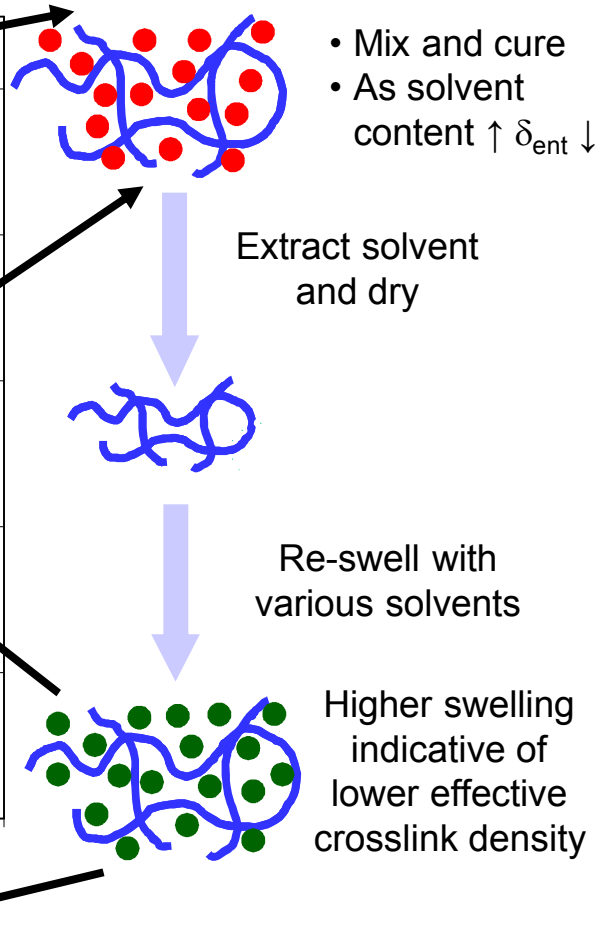
Blue – "Extracted"

Cure polymer and solvent together and extract solvent leaving elastomer



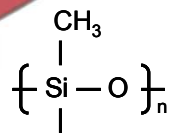
Swelling of Polybutadiene Networks



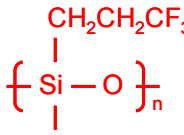


- As initial BEHS concentration increases, entanglements are screened, and network has more open structure
- Exploit technique in stiffer matrix for high porosity scaffolds

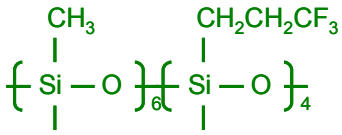
Transition to Silicones



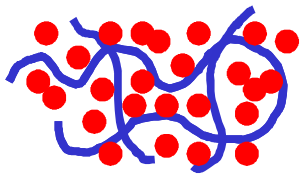
DC 3-6635

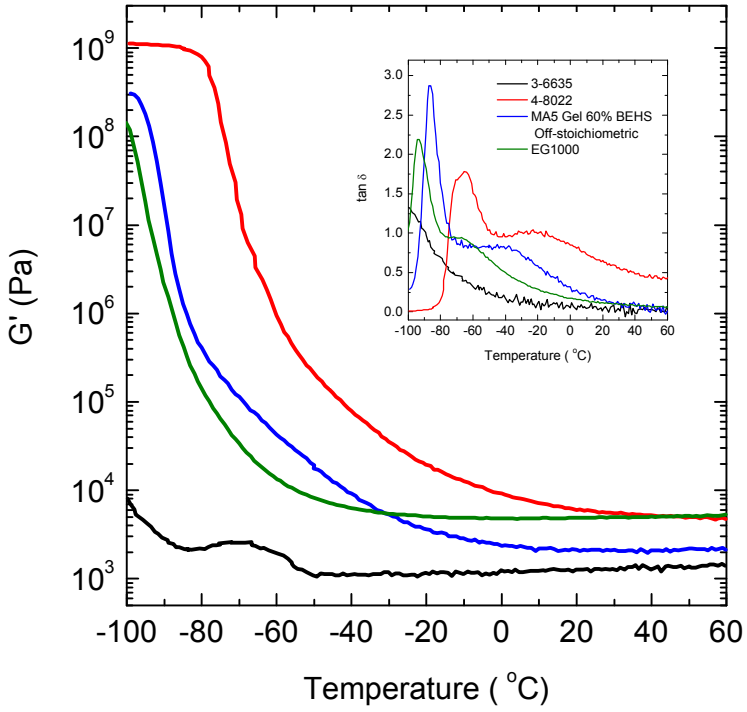


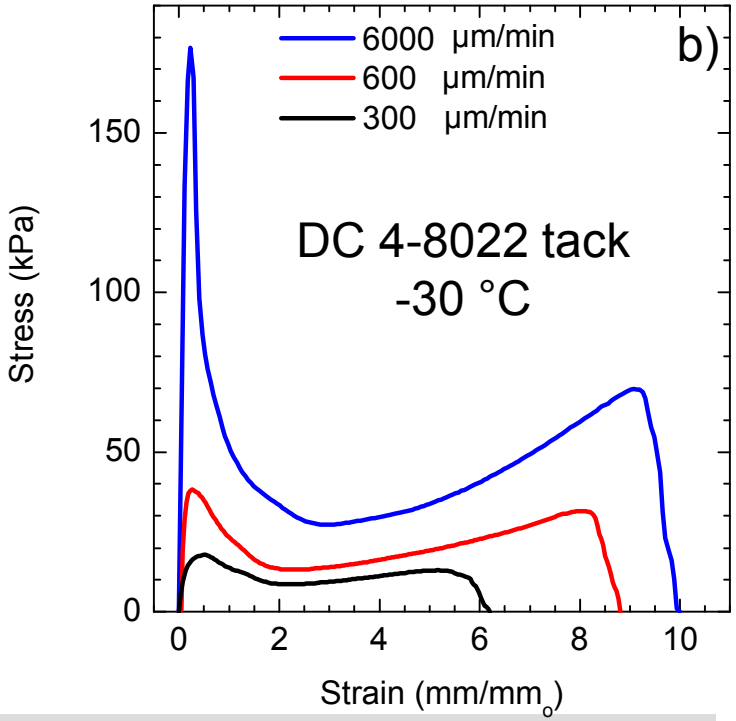
DC 4-8022



EG 1000



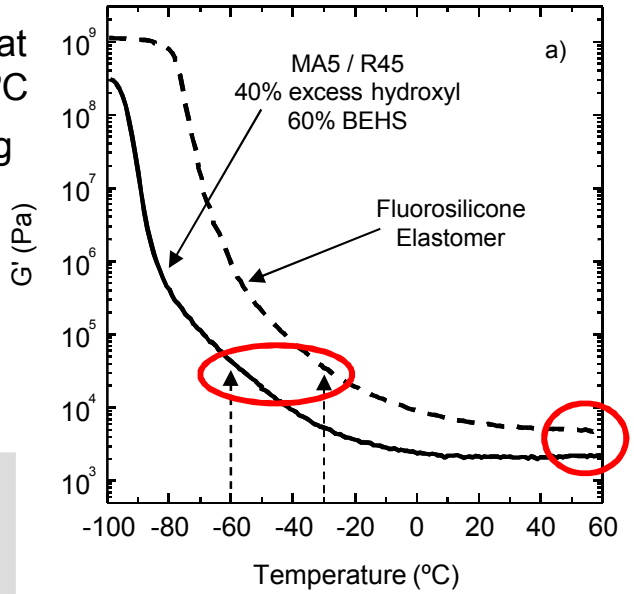


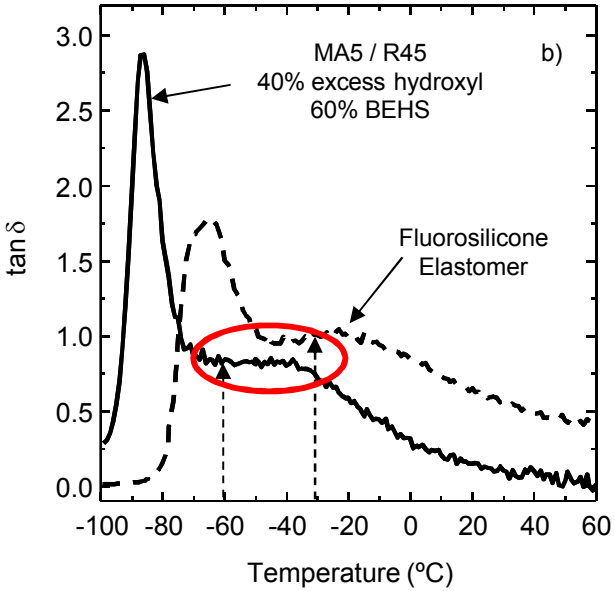


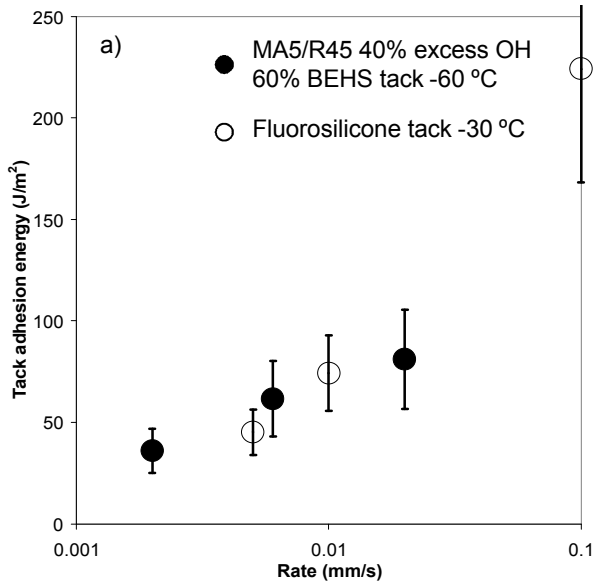
1. Polybutadiene gels will not meet lifetime requirements
2. Silicones have excellent chemical stability over device operating range
3. Copolymer and fluorosilicone gels exhibit:
   - High sol content
   - Plateau region G' < 10^4 Pa
   - High value for low temperature tan δ
   - Extension and fibrillation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

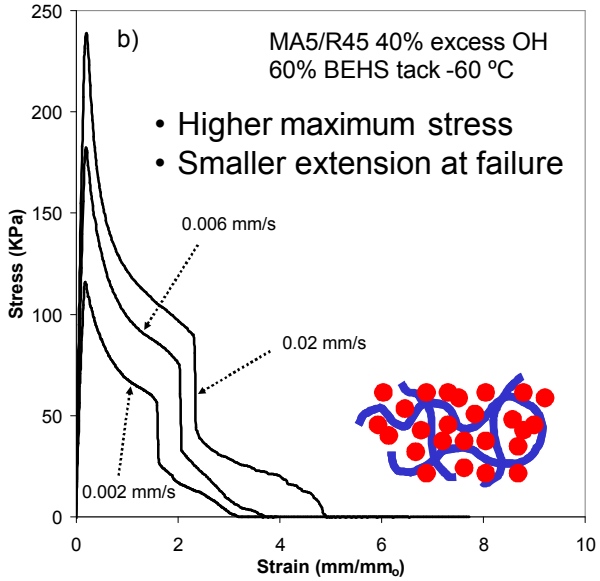
Silicone – PBD Gel Comparison

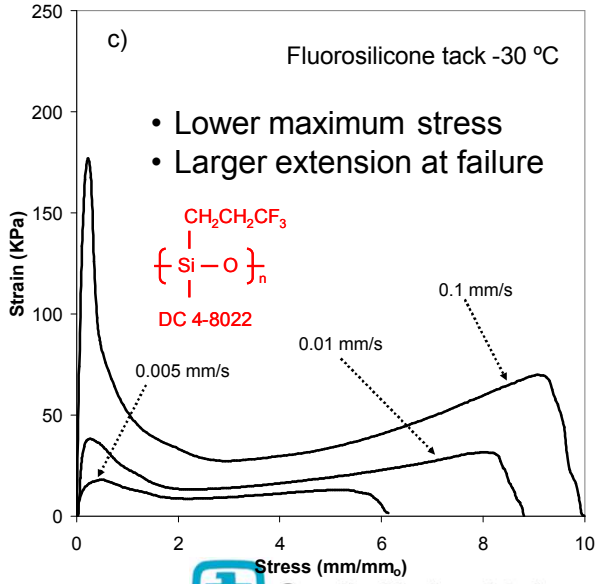
1. Compare fluorosilicone elastomer at -30 ºC with BEHS/PBD gel at -60 ºC
   - Same temperature relative to Tg
   - Same G' at temperature
   - Same tan δ at temperature
   - Same plateau G'
   - Same sol fraction
2. Same tack adhesion energy (integral of stress-strain)
3. Very different stress-strain shape
4. Is this due to large sol size in fluorosilicone gels?









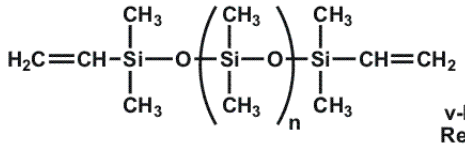


Sandia National Laboratories

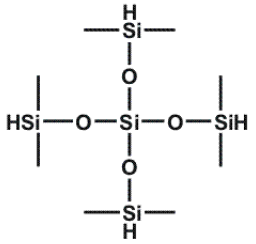
Impact of Sol Size

Can high Mw sol represent a long term risk for adhesive aging?

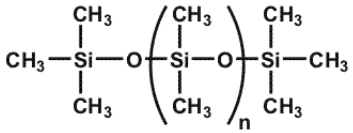
1. What sol fraction is optimal?
   - Too low – poor adhesion / mechanical properties
   - Too high – long term aging risk
2. How do subtle chemical variations in sol and crosslink density impact phase behavior?
3. How fast does sol migrate?
4. How do these depend on sol size?



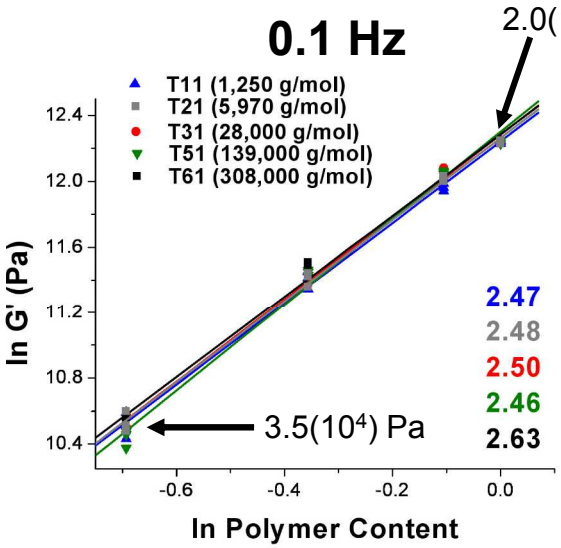
v-PDMS
Reactive
Vinyl Terminated PDMS

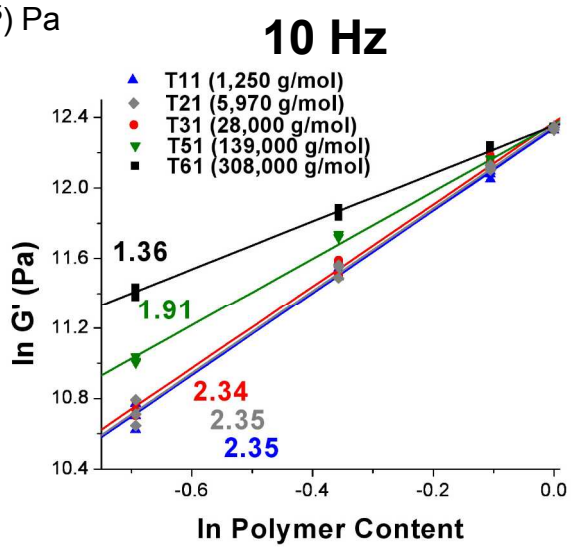


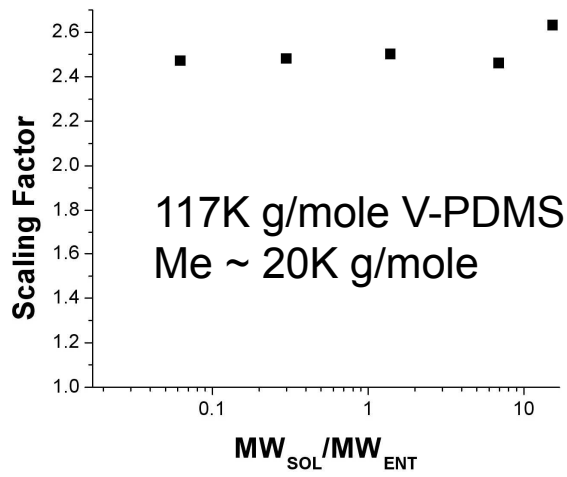
Tetrafunctional
Silane Crosslinker

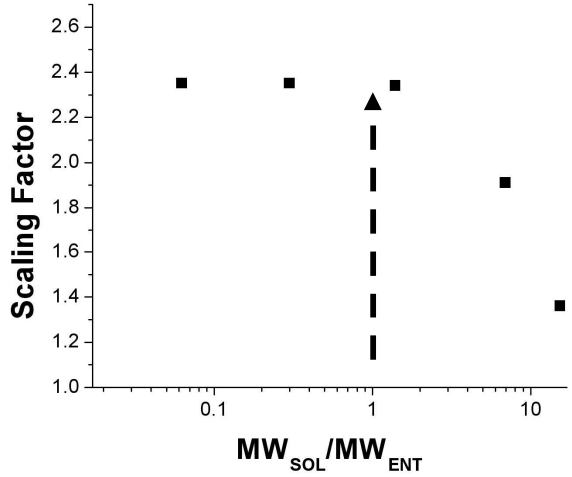


m-PDMS
Non-reactive
Methyl Terminated PDMS







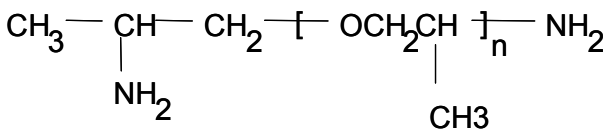


- Scaling factor depends on sol Mw and frequency
- Low frequency everything behaves as small molecule
- Can we separate sol mobility from micro-structural differences?
- Measure rheology on extracted gels

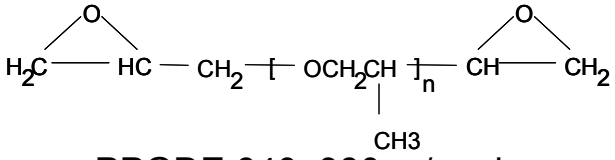
Sandia National Laboratories

Epoxy Gels: Impact of Monomer Size

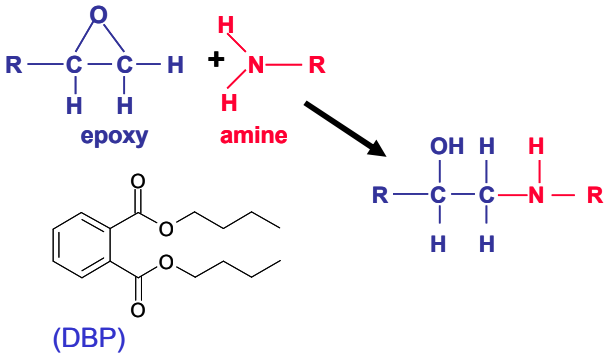
Epoxy

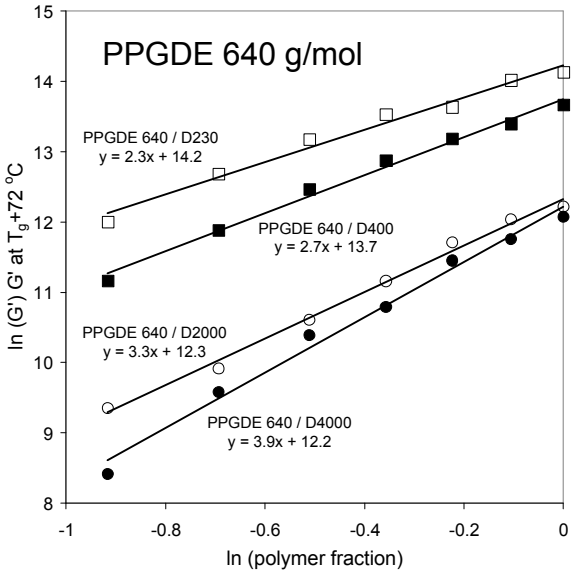


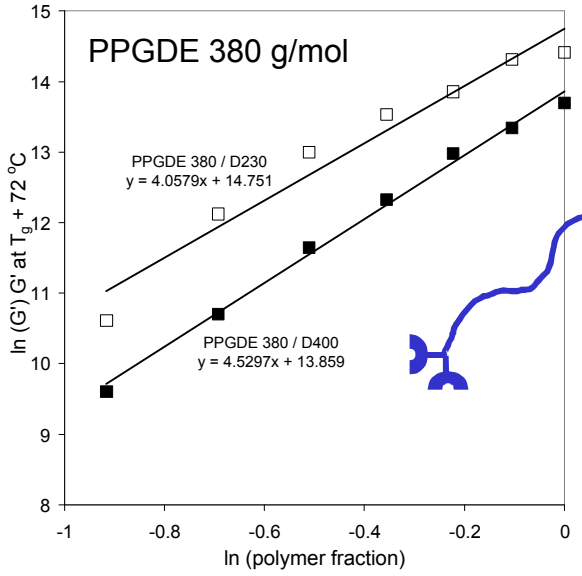
4000, 2000, 400, 230 g / mole



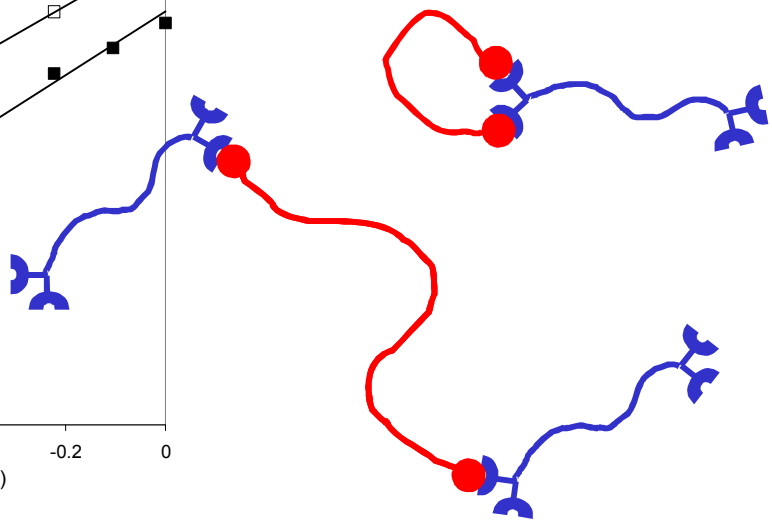
PPGDE 640, 380 g / mole







1. Scaling exponent increases with increasing Mw of diamine
2. Scaling exponent increases with decreasing Mw epoxide
3. Scaling exponents are much larger than what is observed with PBD or silicone gels
4. Loop formation “bite-back” reaction (rather than entanglement screening)



General conclusion:

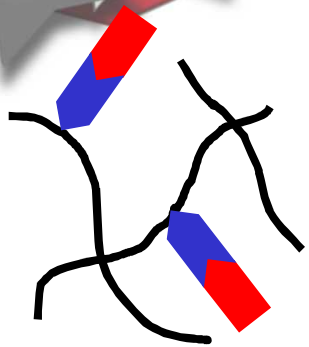
- entanglement screening when monomer Mw > Me
- loop formation when monomer Mw < Me

Processing Development

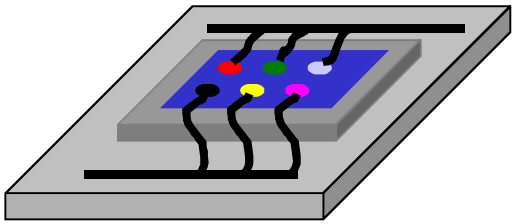
- Designed gel materials for functional devices
- Designed processing capability (small lab-scale, pilot scale, full production scale-quality processing)

- 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



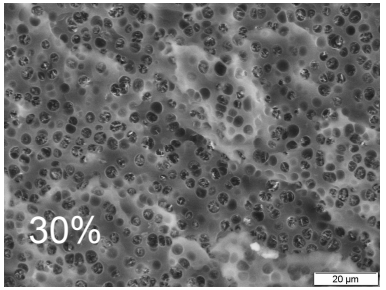
Develop specific agent – receptor binding sites

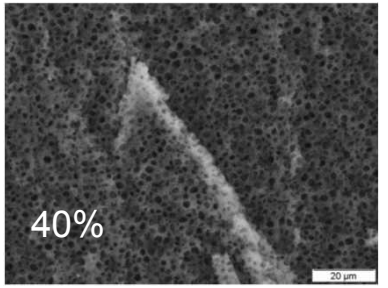


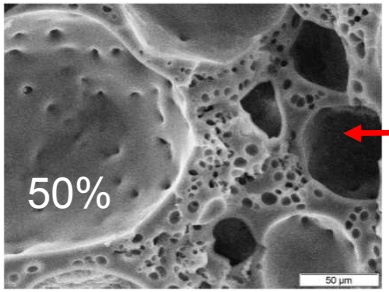
Develop functional sensor devices / arrays

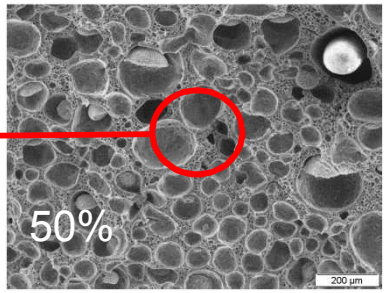
1) Sensor Opportunities

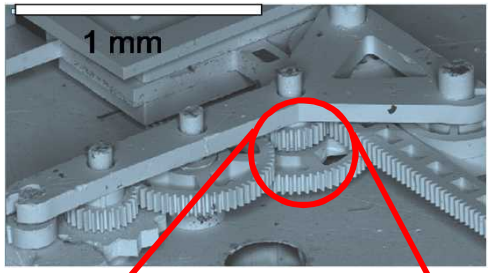
- Changes in equilibrium swelling
- High porosity scaffolds and "molecular templating"

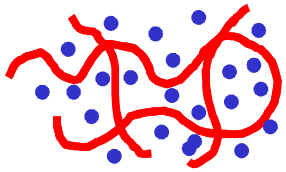


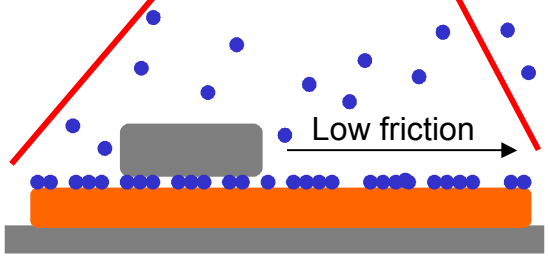




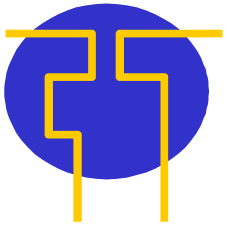








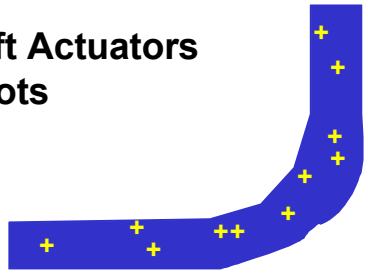
2) Self-Healing Lubrication Layers



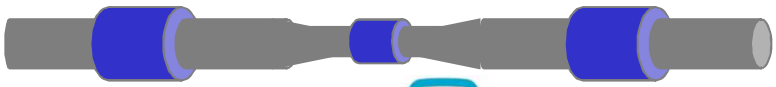
3) Stretchable electronic circuitry

4) Micro-devices / Soft Actuators Flexible Robots

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

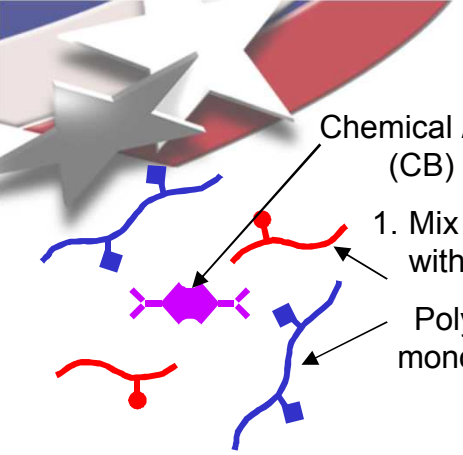


Micro-scale pumps, valves, switches, motors driven by electrical or magnetic fields



Sandia National Laboratories

Engineered Nano-sponge for Chemical and Biological Detection



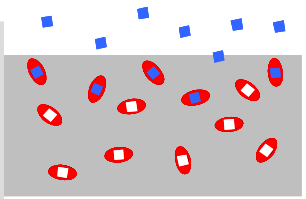
Chemical / biological (CB) agent

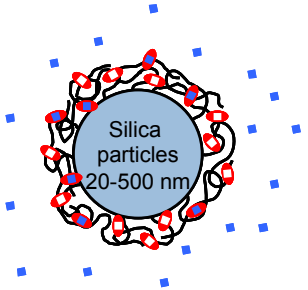
1. Mix CB / template with monomers

Polymer monomers

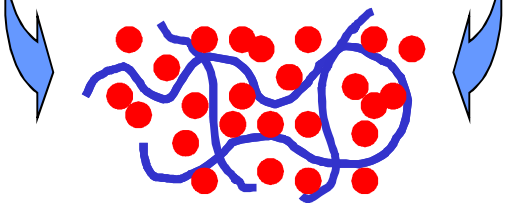
Polymer Nano-Sponge Sensor

1. High porosity scaffolds
2. Complex formation
3. Molecular templating



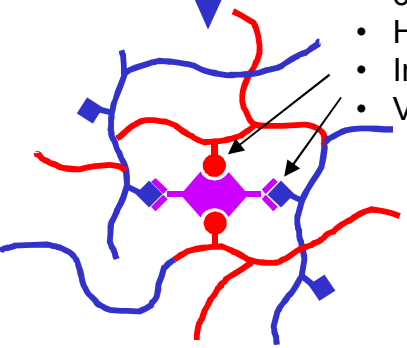


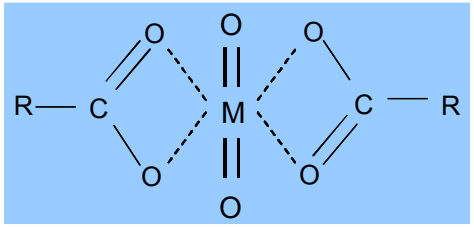
Couple bulk and thin film technology into high porosity polymeric scaffolds



2. Cure polymer around template

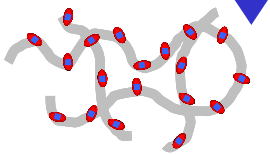
- covalent bonding
- Hydrogen bonding
- Induced dipole
- Van der Waals

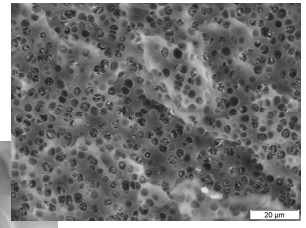


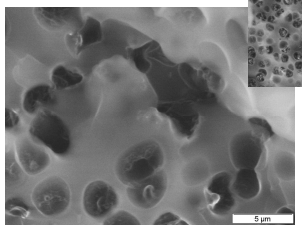


3. Chemical interactions induce polymer structure around template

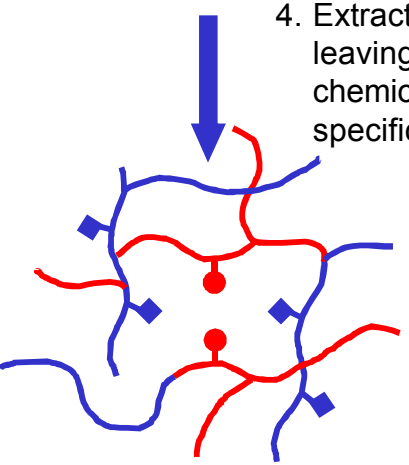
Extract solvent from polymer gels leaving porous structure







4. Extract template leaving physical and chemical memory specific for CB agent



Alternative applications

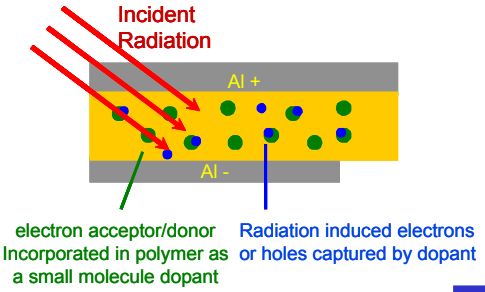
- Exploit templating / porous materials approach to engineer controlled structures
- Utilize alternative external forces such as self-assembly, shear, electric/magnetic fields for additional microstructure control

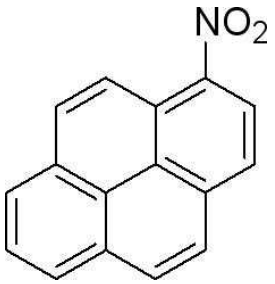
Control porosity through polymer-solvent interactions, solvent loading, cure kinetics

Summary & Conclusions

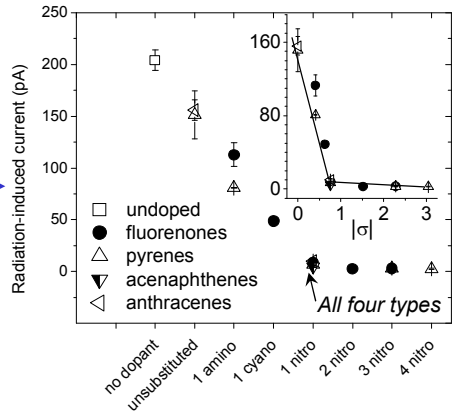
- Developed non-aqueous gels that perform over broad temperature range (polybutadiene, silicone, epoxy based gels)
  - Flexible polymer backbone
  - Low volatility solvent
  - Polymer solvent miscibility
  - Energy dissipating defects
- Entanglement screening and loop formation scaling phenomena
- Implemented 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

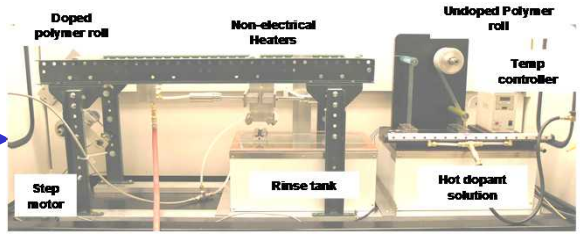
Device Functionality in Radiation Environments: Radiation Tolerant Polymer Films





Nitropyrene (NP)



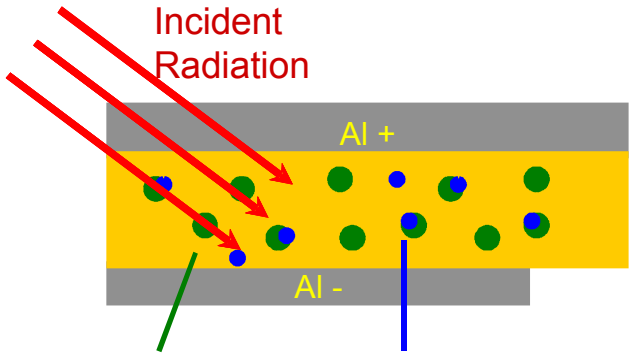


Chemistry and microstructure → Material properties → Process design and implementation

Sandia National Laboratories

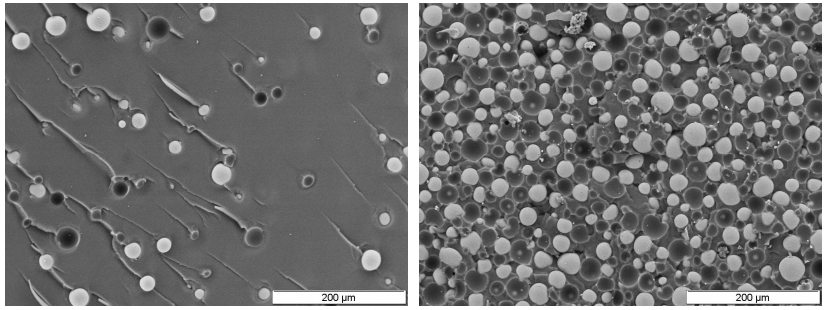
Two Approaches for Radiation Tolerant Devices

1. ***Engineer radiation tolerant polymers for the device***



- 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

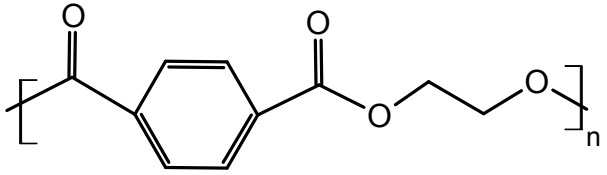
2. ***Develop polymeric composites to shield devices from radiation exposure***



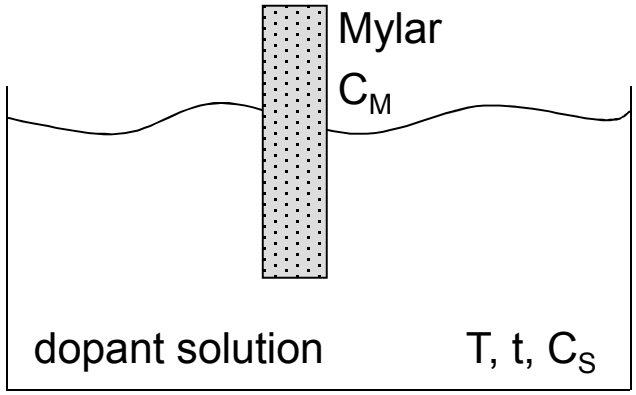
- High-Z particulate fillers with polymeric matrix for low density shielding composites
- Loadings from 1 to 50 volume % depending on radiation environment
- Localized "Spot" shielding of sensitive components / devices

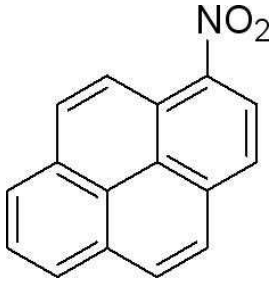
What Makes a Good Electron Trap?

- 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

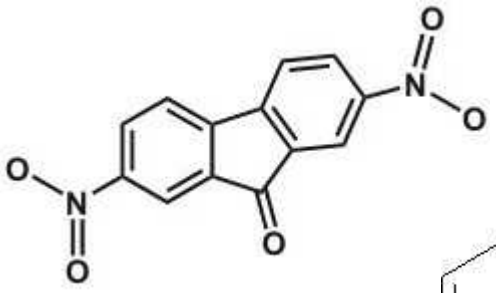


Poly(ethylene terephthalate) (PET)

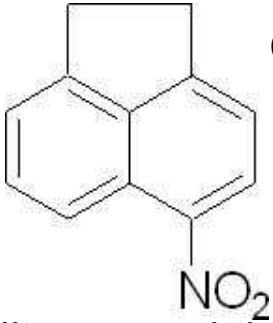




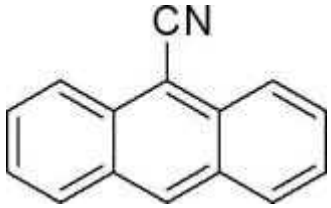
Nitropyrene
(NP)



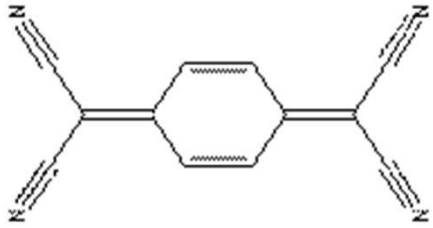
Dinitrofluorenone
(DNF)



Nitroacenaphthene
(NAN)

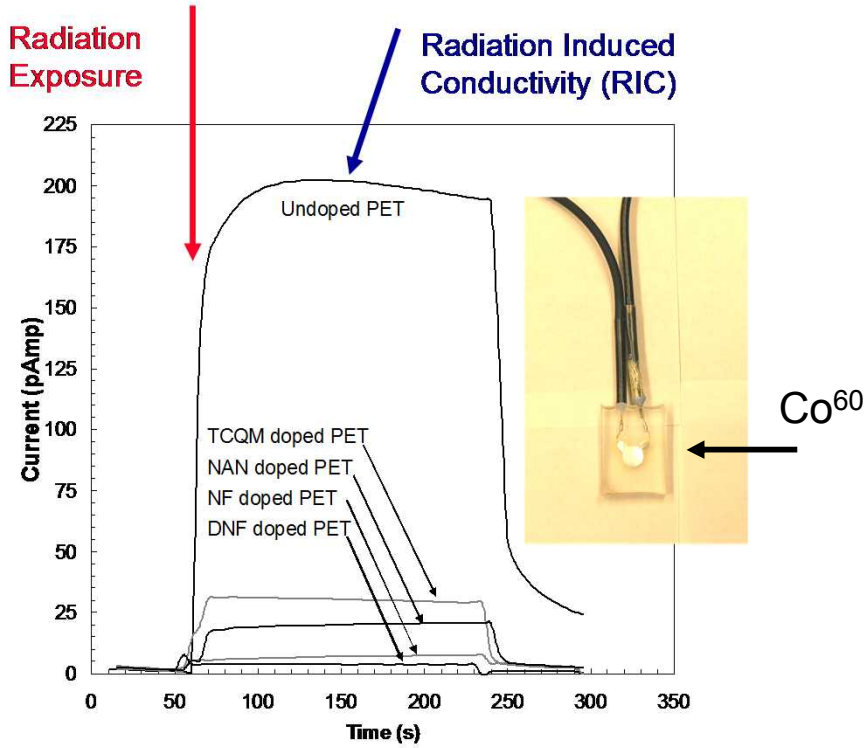


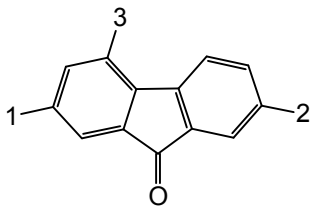
Cyanoanthracene
(CAN)

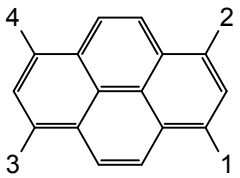


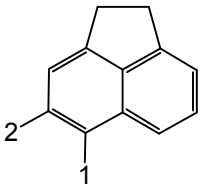
Tetracyanoquinodimethane
(TCQM)

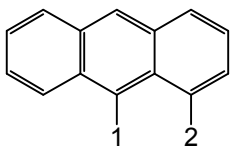
RIC Testing and Conclusions




Fluorenone compounds

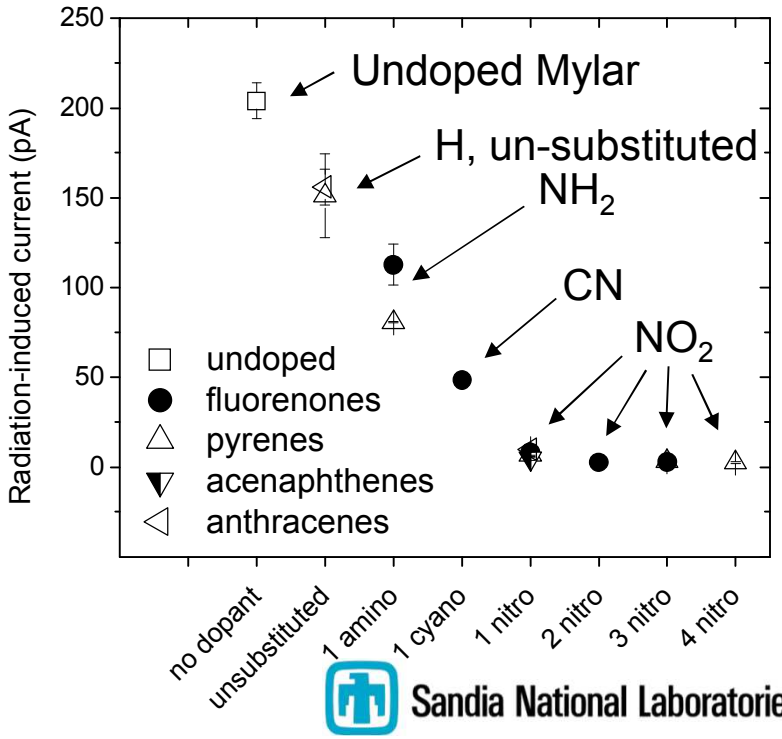

Pyrene compounds


Acenaphthene compounds


Anthracene compounds

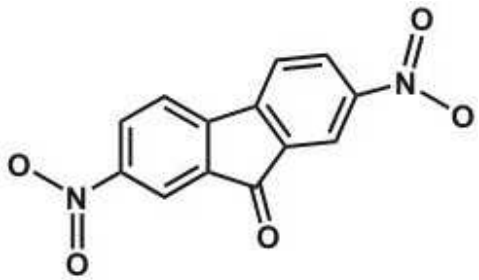
Conclusions:

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

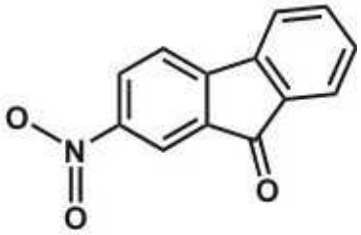


Sandia National Laboratories

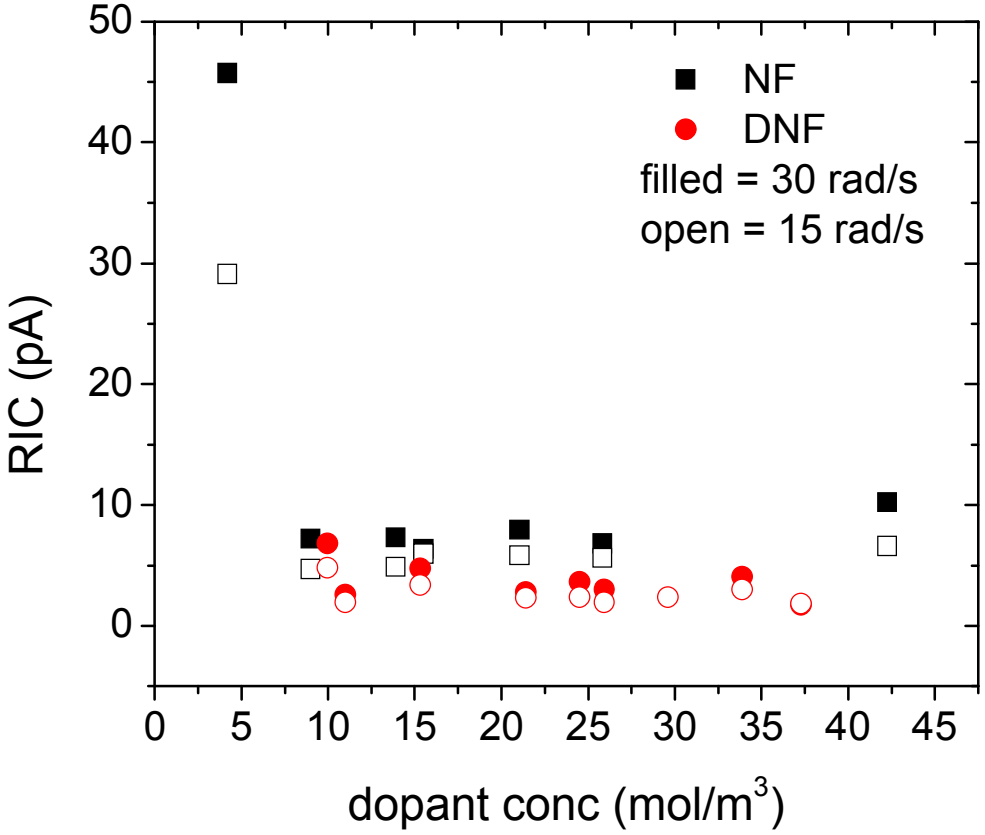
RIC Dependence on Dopant Concentration



2,7-dinitro-9-fluorenone (DNF)



2-nitro-9-fluorenone (NF)

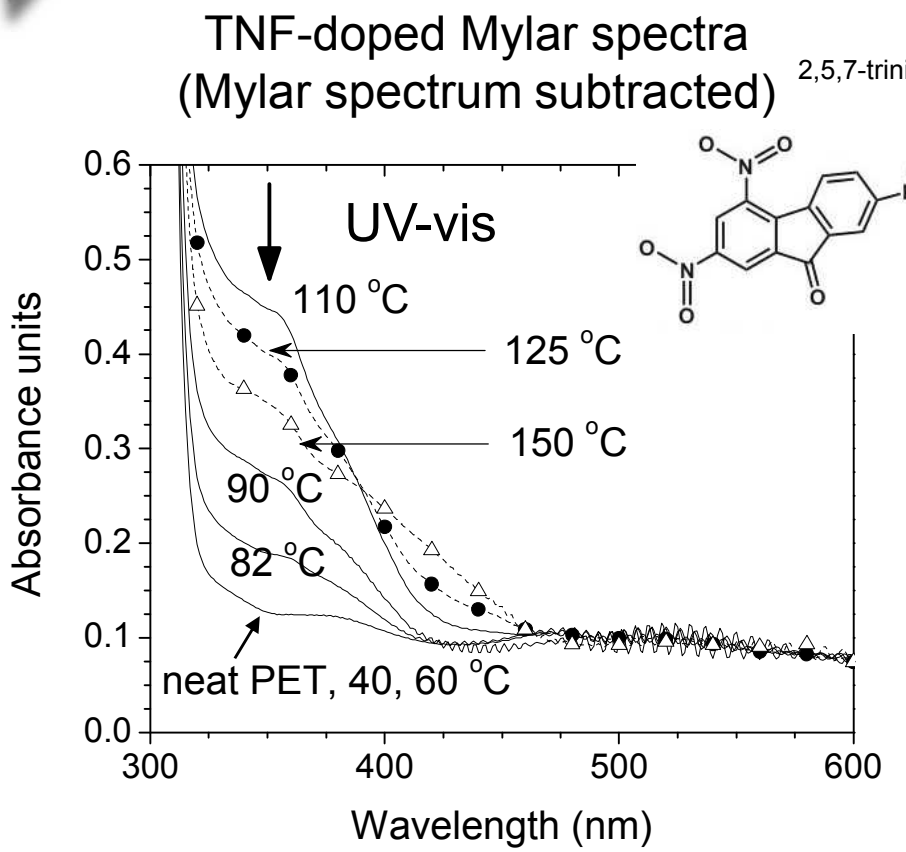


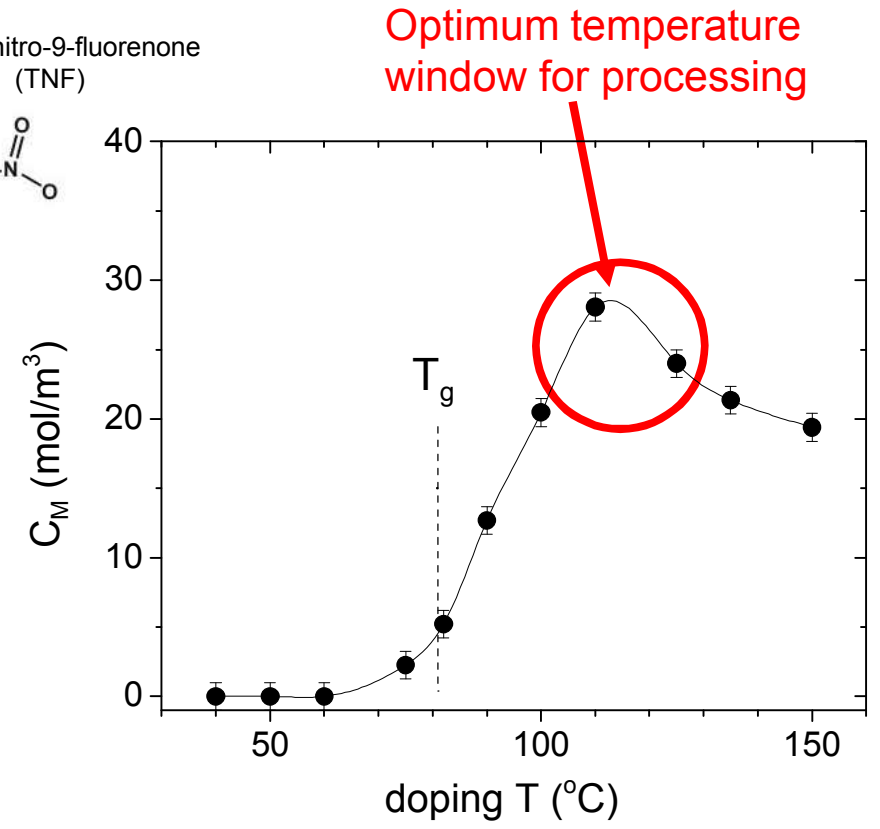
Conclusions:

1. Optimum RIC reduction with dopant concentration
2. Dopant concentrations above 10 mol/m^3 in Mylar result in constant RIC values
3. Order of magnitude away from RIC increases with increasing dopant
4. Broad dopant concentration window ensures robust processing / RIC performance

Sandia National Laboratories

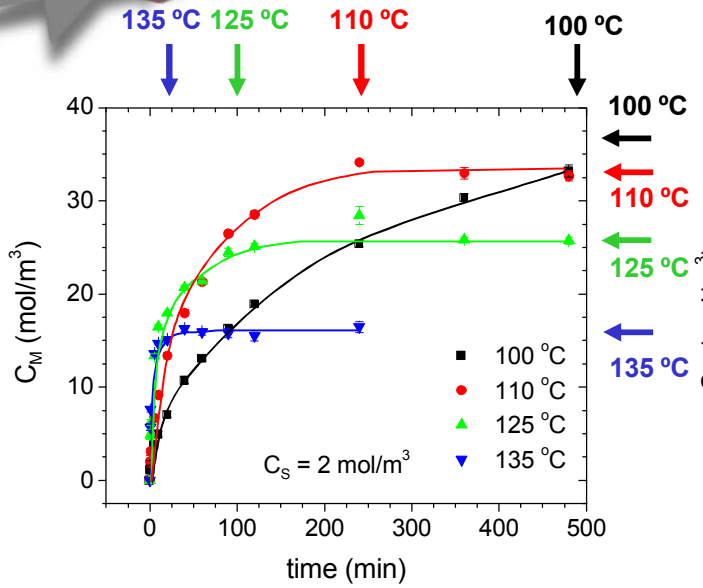
What Controls Dopant Uptake in Polymer Film?

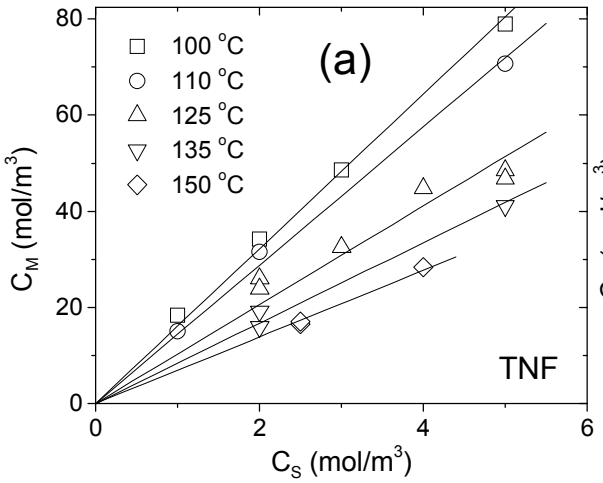


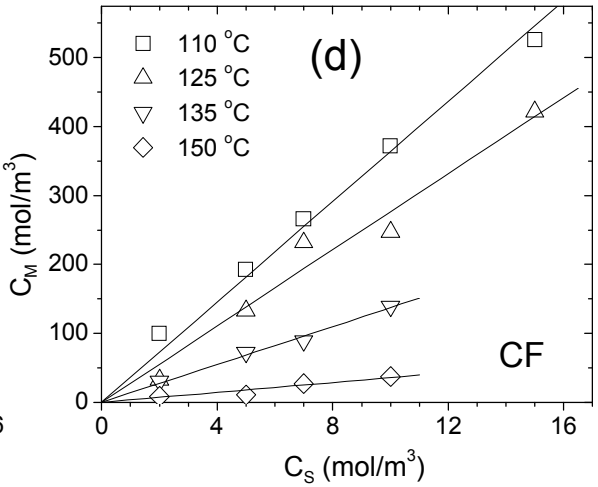


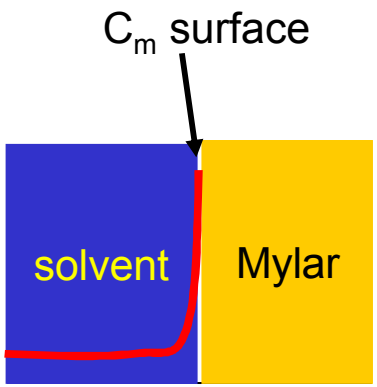
- Surface adsorption / Diffusion phenomena controls dopant concentration in Mylar
- Competing effects
  - Temperature increases diffusivity
  - Temperature decreases amount of surface adsorbed dopant
  - Optimum processing temperature window

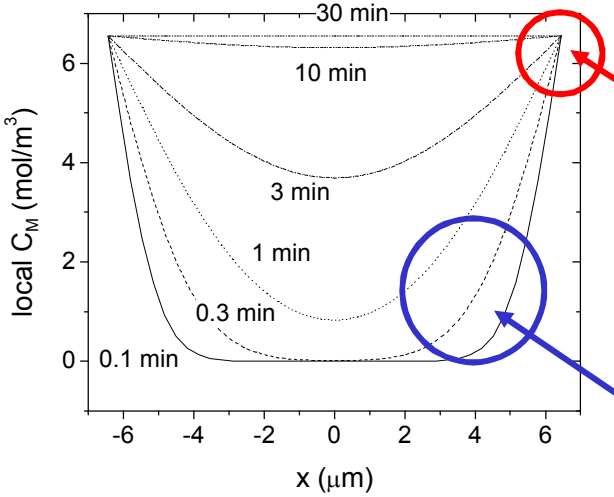
An Adsorption / Diffusion Process











Langmuir Adsorption

$$C_{ds} + C_{vM} \underset{K_a}{\longleftrightarrow} C_{dM}$$

$$C_{dM} = \frac{C_{ds} C_T}{C_{ds} + 1/K_a}$$

Fickian Diffusion

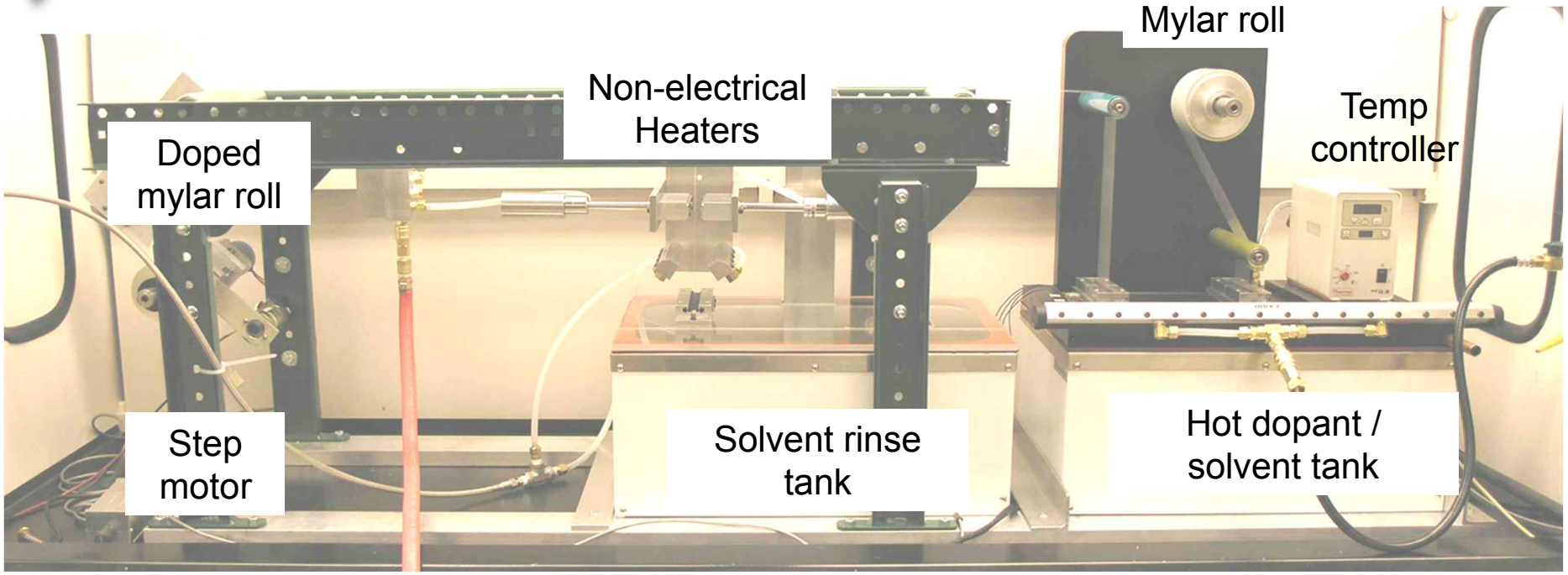
$$\frac{\partial}{\partial x}\left(D \frac{\partial C_M}{\partial x} \right) = \frac{\partial C_M}{\partial t}$$

Dopant adsorbs on film surface

Dopant diffuses through film

Sandia National Laboratories

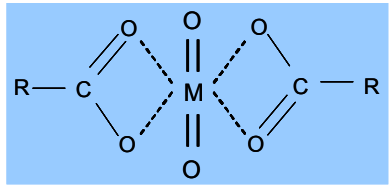
Process Development / Component Testing



- 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

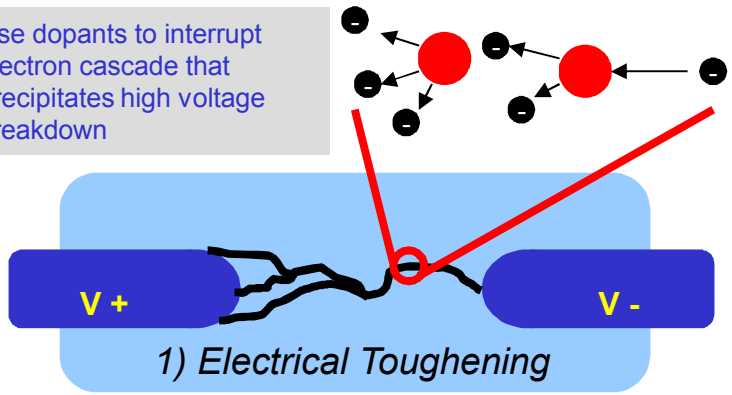
Summary & Conclusions

- 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

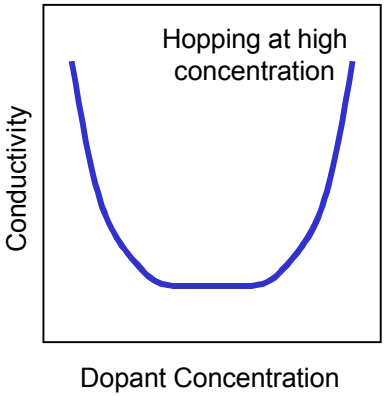
Use dopants to interrupt electron cascade that precipitates high voltage breakdown



1) Electrical Toughening

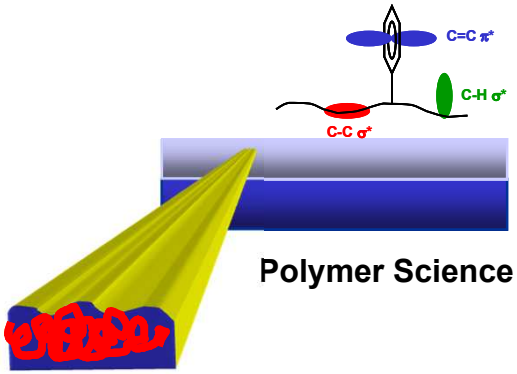
2) Potential alternative applications for doped polymers

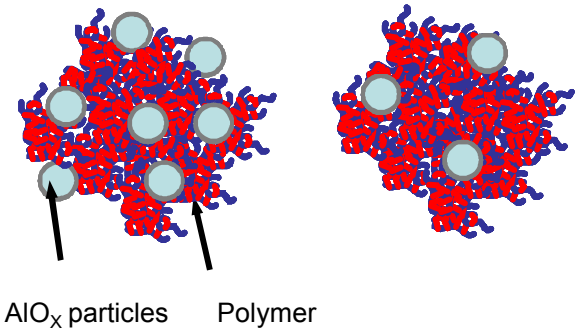
a. Molecular / organic electronics
b. Anti-static coatings
c. Conductive / non-conductive filler coatings
d. Nano-wires / conductive fibers

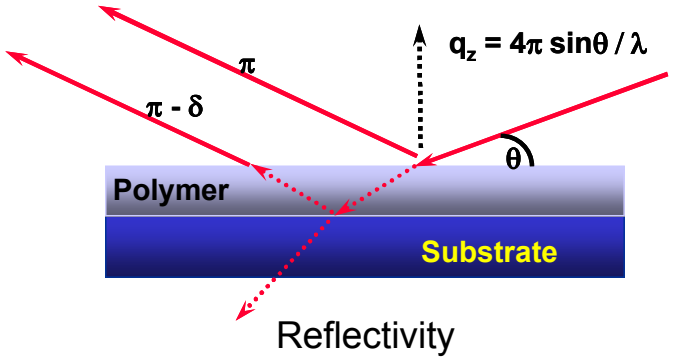


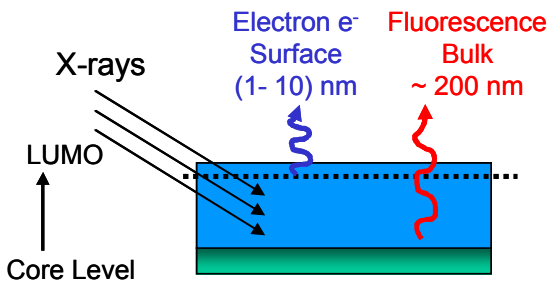
Sandia National Laboratories

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



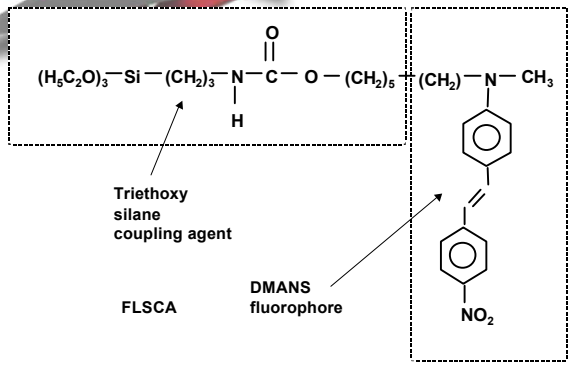




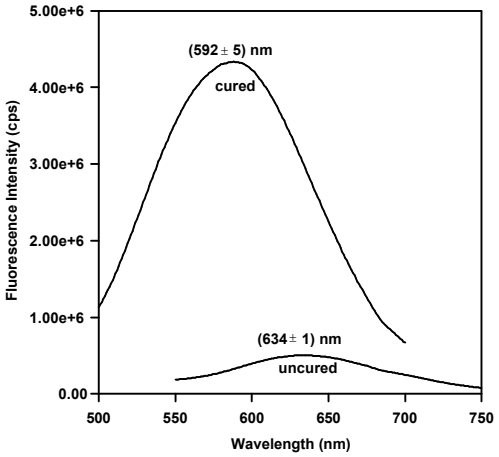


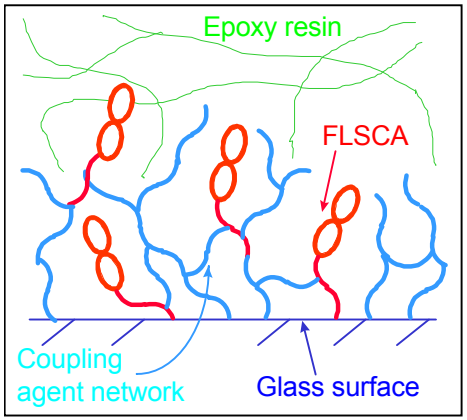
Sandia National Laboratories

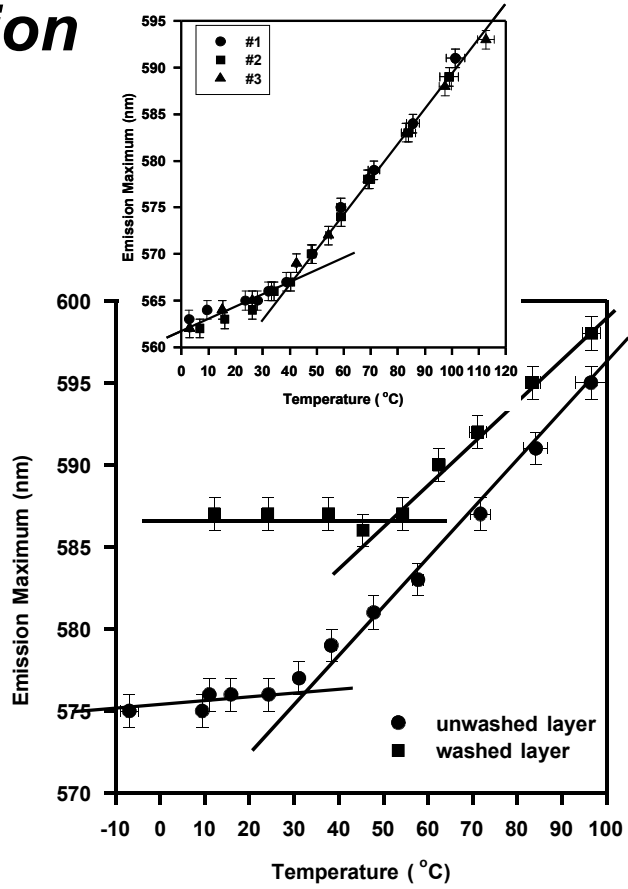
Localized Fluorescent Response for Interfacial Characterization

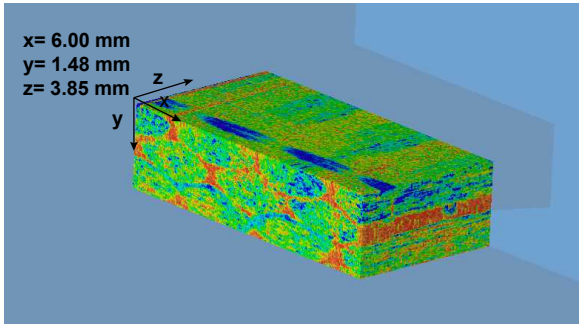


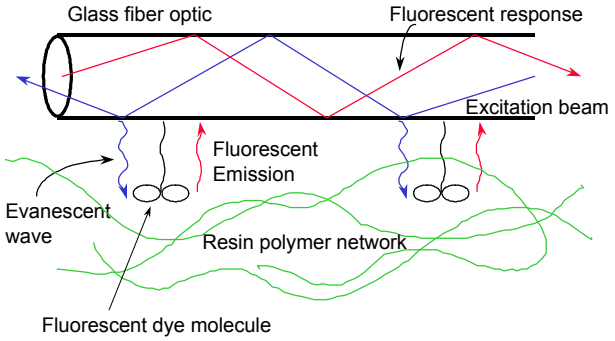
- Fluorescently labeled silane coupling agent (FLSCA) grafted to glass in mixed silane layer
- Blue shift in emission and intensity increase during resin cure
- Sensitive to resin-silane layer interpenetration
- Sensitive to interfacial Tg





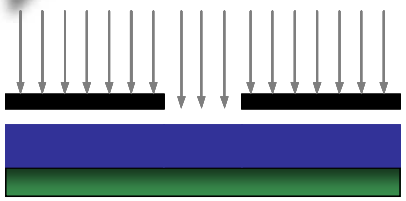




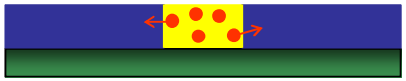


- Grafted FLSCA to glass fiber-optic and demonstrated proof-of-concept for processing sensor
- Monitor cure during composite processing
- Monitor resin flow
- Monitor resin impregnation into fiber tows

Interfaces in Photolithography

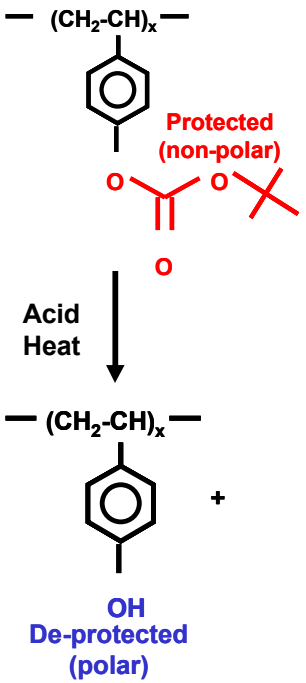


Apply and Expose



Bake, Diffuse, and React

Develop



Surface and bulk chemical differences in photoresist

- PAG surface segregation
- reaction rate differences

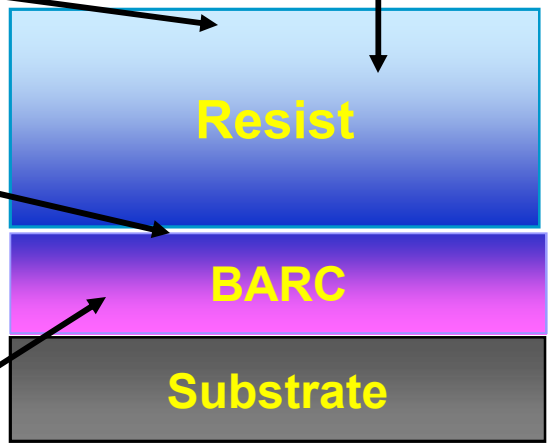
BARC – resist interface

- resist interpenetration into crosslinked BARC
- diffusion of unreacted BARC components

Characterization of BARCs

- thin film properties
- surface chemistry
- processing

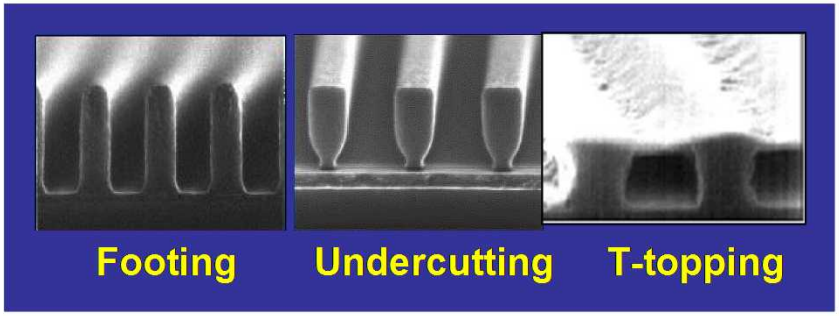
Properties of thin resist films

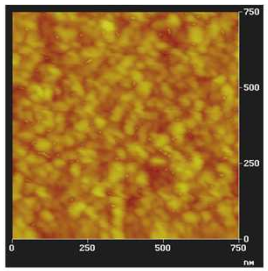


Chemical characterization of model line edge region

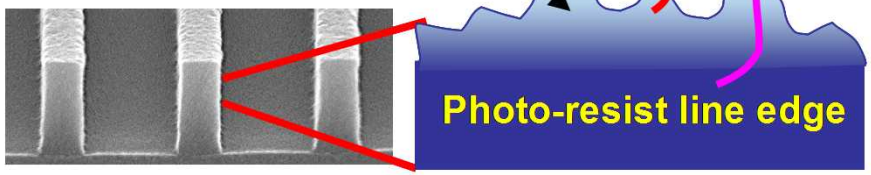
- deprotection profile after development
- model development
- extent of deprotection at interface depended on processing conditions

What are the physical / chemical factors that lead to pattern deviations near an interface?

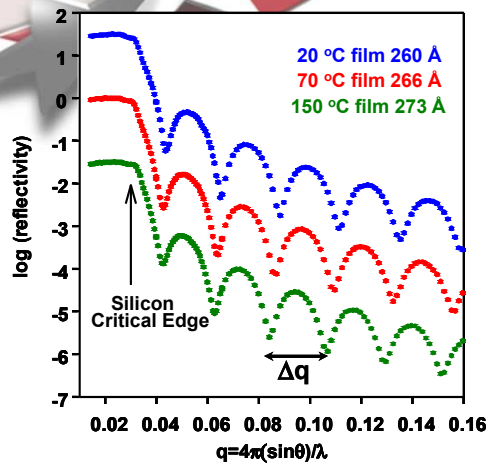


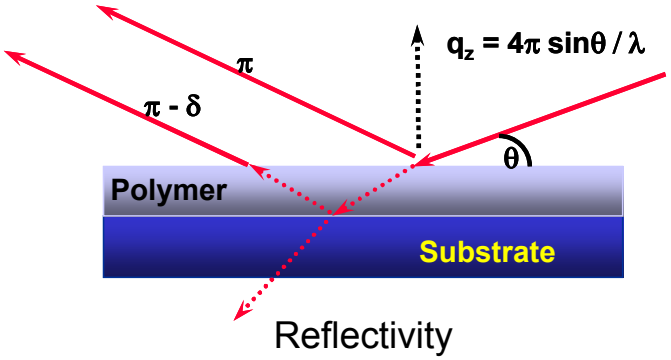


NEXAFS Reflectivity



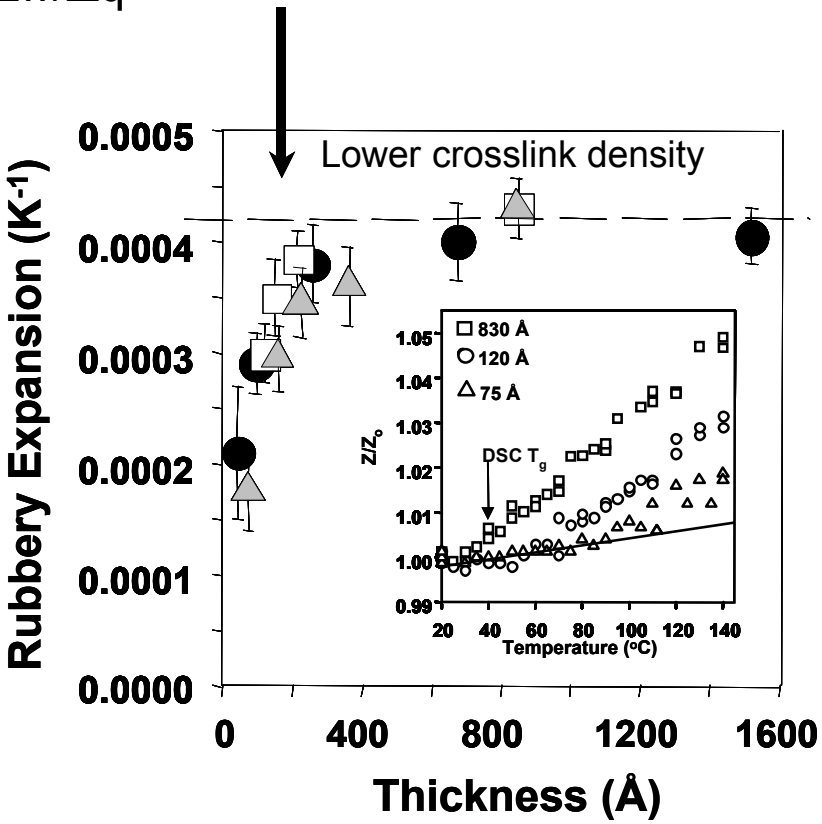
Polymer Thin Films and Interfaces

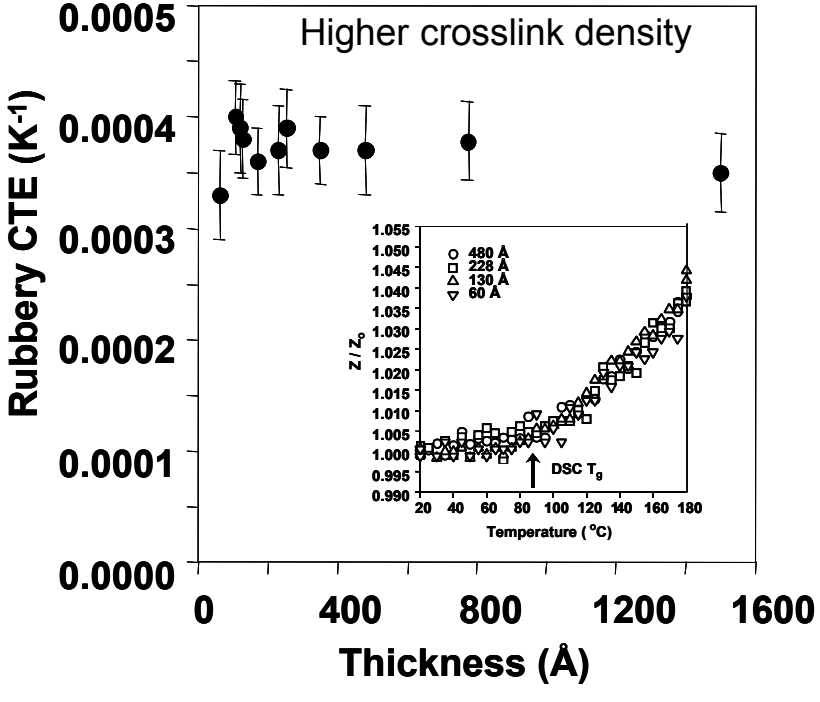




- X-ray reflectivity to accurately measure thickness of thin films
- Loosely crosslinked (Tg~40ºC) films exhibited glassy expansion well above bulk Tg and decrease in rubbery CTE with film thickness
- Changes in thermal properties were independent of surface treatment
- Highly crosslinked films (Tg~90ºC) did not exhibit a change in thermal properties

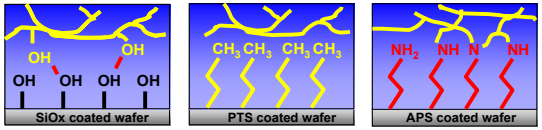
$t=2\pi/\Delta q$ **10 crosslinks**

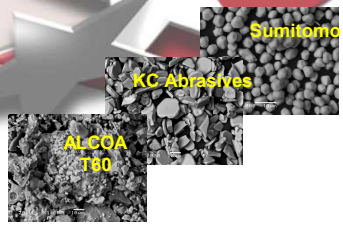


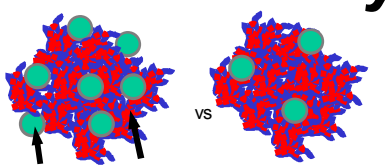


Polymer Composites

1. Encapsulants



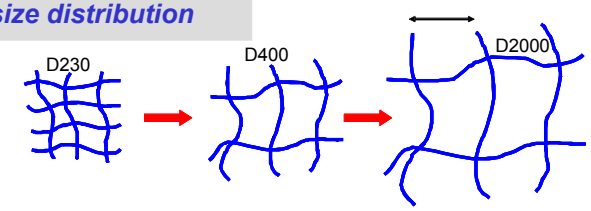




AlO_X particles Polymer

1) Particle shape, size, and size distribution

2) Filler loading



3) Polymer crosslink density

Conclusions

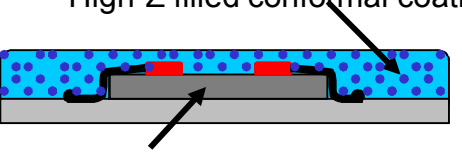
- Alumina-epoxy composites are robust
- Variable changes have minimal impact on cured properties
- Viscosity is sensitive to shape / size / distribution / loading
- Relax materials specifications
- Processing is key

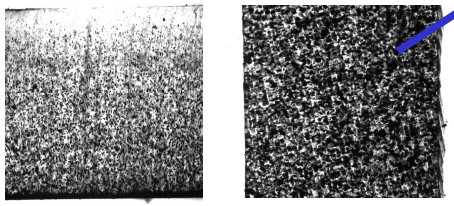
4) Filler surface chemistry

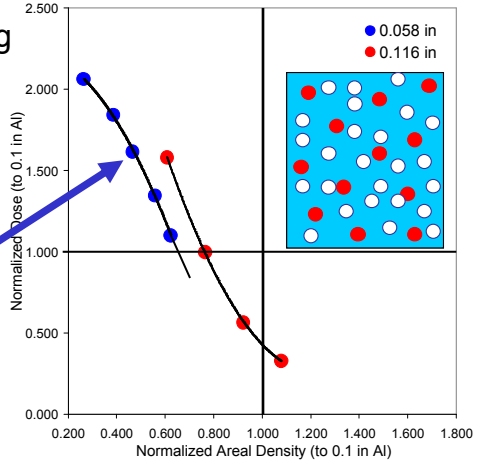
Future

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

2. Radiation Shielding







Results / Goals

- 35% mass reduction
- > 50% mass reduction

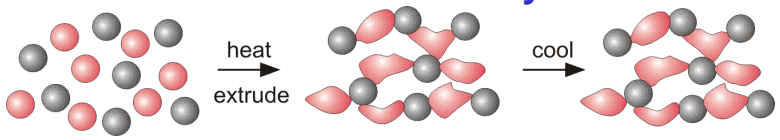
Challenges

- Particle settling (conductivity)
- Transparency in thin films

Solutions

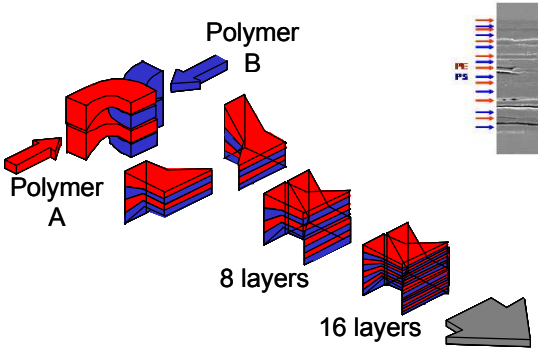
- Sub-micron / nano-particles
- Insulating surface coatings
- Low density fillers
- Localized or global

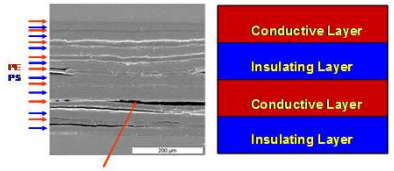
3. Conductivity

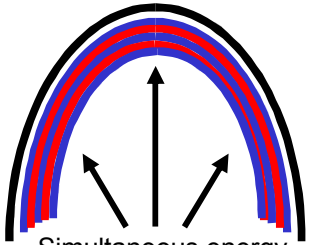


Results

- Solid filler with low melting filler (10 μm to 100 nm)
- Conductivity consistent with percolation (1-10 Ω·cm)
- Processable viscosity
- Sub-micron and nano-particles for future applications

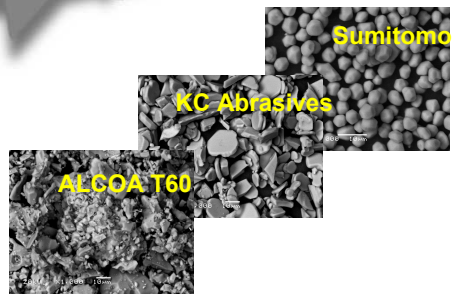


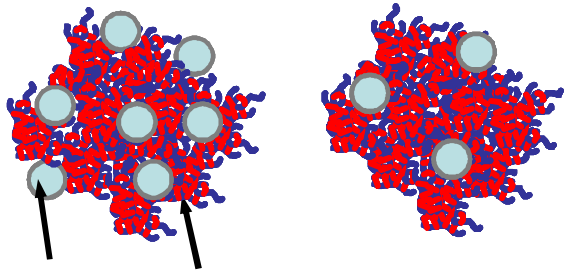




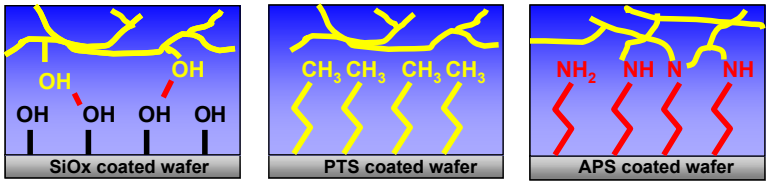
Simultaneous energy storage and radiation shielding

Sub-Micron and Nano-Particulate Composites





Application targets and processing issues drive research

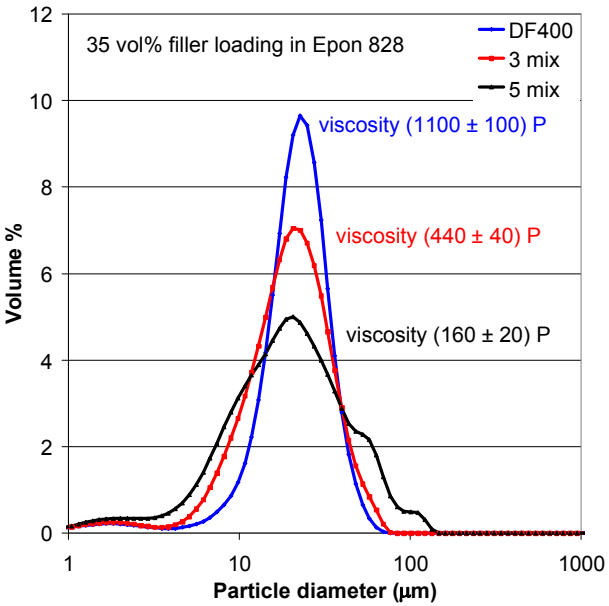


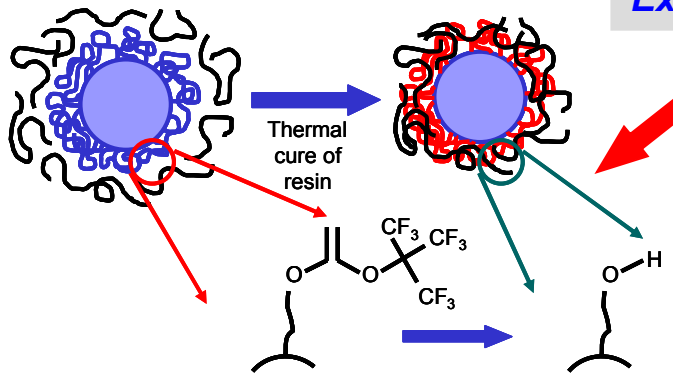
1) Control particle shape, size, size distribution

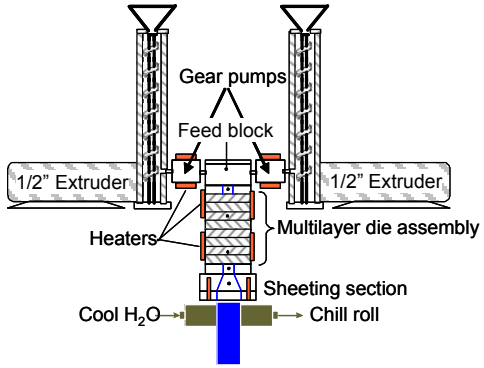
2) Utilize lowest filler loading to obtain desired properties

3) Modify filler surface chemistry to "control" particle agglomeration. Exploit "engineered coatings"

Broadening particle size distribution leads to decrease in resin viscosity





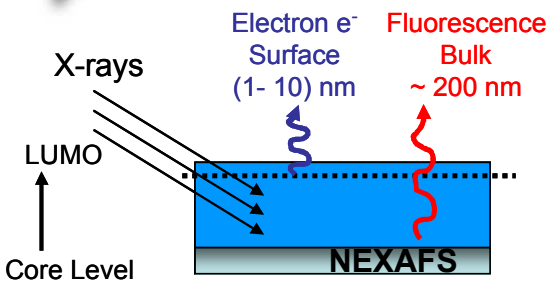


Engineered Coatings

1. **Switchable coatings / structural**
   - Initial coating with low friction / weak polymer interactions (viscosity reduction)
   - Final coating with strong polymer interaction (promote adhesion)
2. **Conductive coatings**
   - Enable controlled agglomeration
   - Rapid electron transport
   - Nitro-aromatic dopants at high loadings?

4) Advanced mixing techniques and extrusion based processing to manufacture high viscosity solutions

Synchrotron Based Interfacial Science

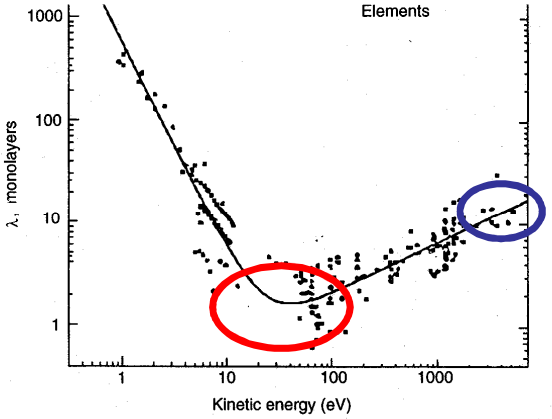


Expanding Beamline Capabilites

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)

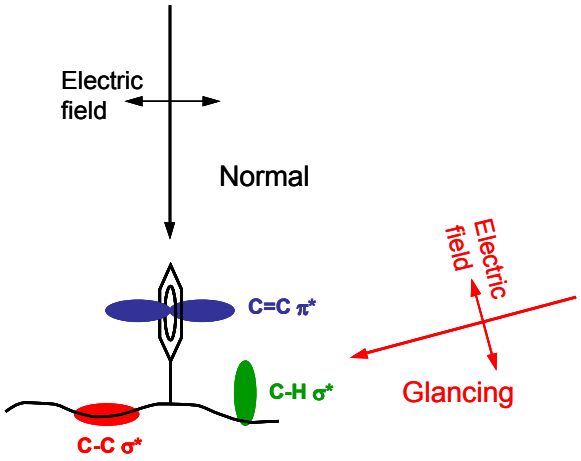


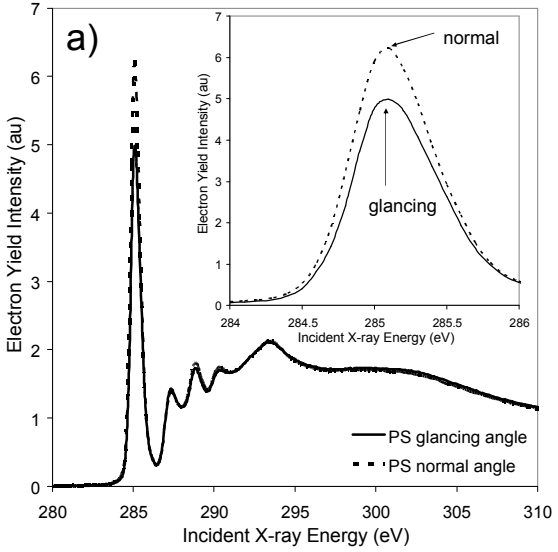
M.P. Shea, W.A. Dench, *Surf. Interface Anal.* , **1**, 2 (1979).

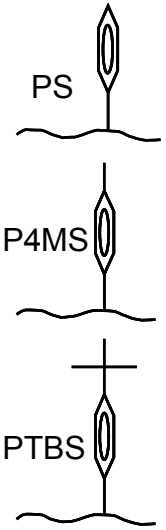
Synchrotron Advantages
- High intensity
- Monochromatic
- Tunable
- Polarized

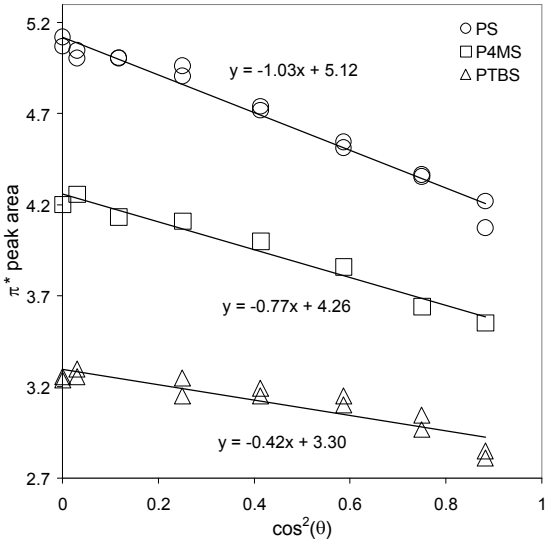
New Measurement Development: Enhanced Depth Profiling Analysis for Composition Gradients and Buried Interfaces

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









Acknowledgements

Primary Collaborators: Phillip Cole, John McBrayer, Lothar Bieg, Ginger DeMarquis

Core Team: Randy Mrozek, Robert Klein, John Schroeder, Shannon Cole, Duane Schneider, Scott Spangler, Michael Belcher, Ron Sanchez, Laura McGrath, Katie Whitaker, Mary Torrez

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.

Composites: Saskia King, Robert Ferrizz, Richard Parnas, Laura McGrath, James Schwank, Ethan Blansett, Diana Wrobel, Gayle Thayer, Gerald Hash, Kevin Austin, Rheka Rao, Lisa Mondy

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 Univeristy, combinatorial research on porous materials)