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The Role of Sol Molecular Weight and Mobility on the Short and Long Term Performance of Polymer Gels

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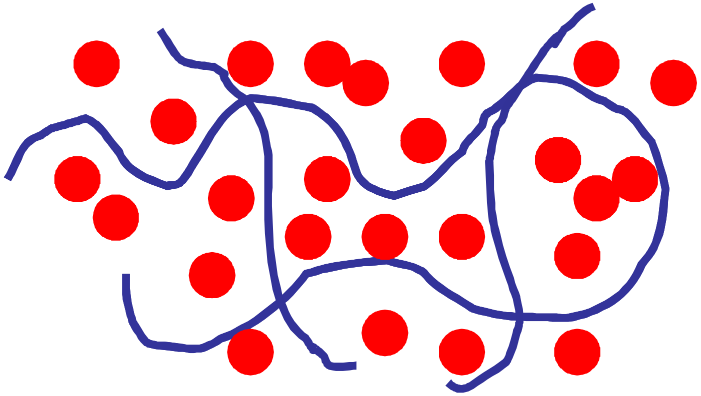
Gel Based Technology

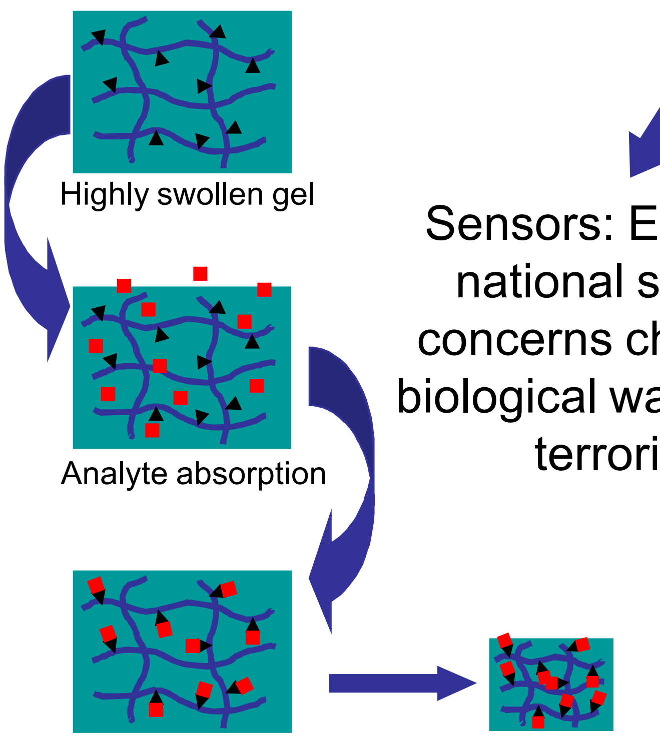
Objective: Design gels to perform over broad temperature range.

- Flexible backbone
- Low volatility solvent
- No polymer or solvent transitions
- Polymer – solvent miscibility
- Good adhesion to a variety of substrates without surface preparation

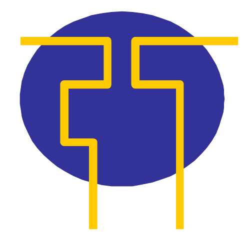


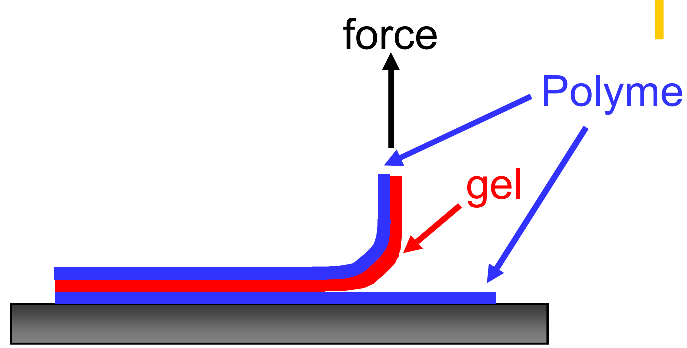
Impact

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



Current Applications: Electronic devices



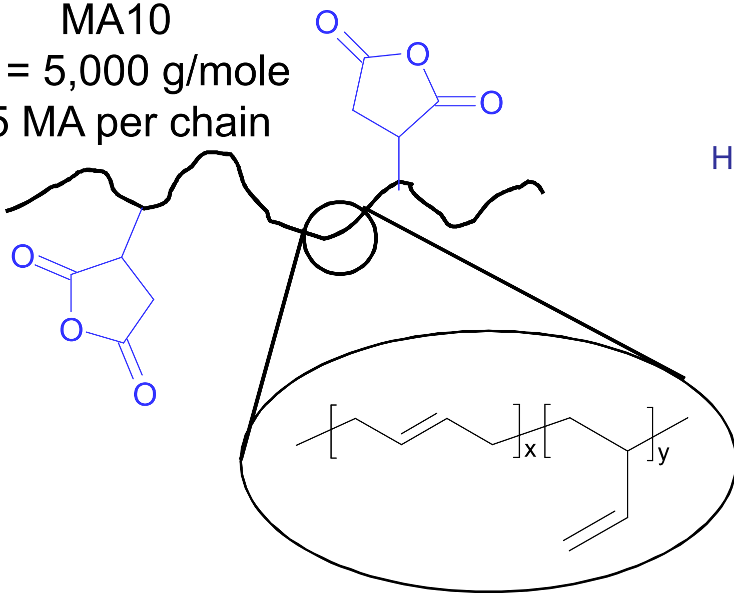


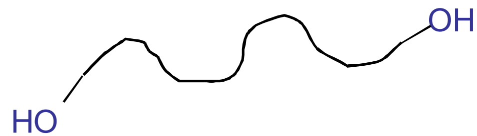
Gel – substrate adhesion is critical for device performance

Initial Gel Formulation (MA10 Gel)

1. Assess whether the gel technology is feasible
2. Determine materials solutions required to improve performance
   - ***Broad temperature requirements (-55 °C to 75 °C)***
   - ***Long lifetime requirements (30+ years)***

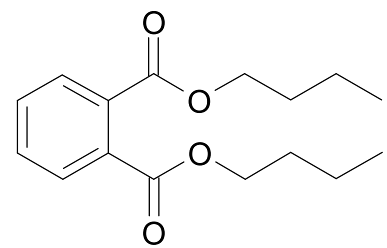
MA10
M_n = 5,000 g/mole
~5 MA per chain



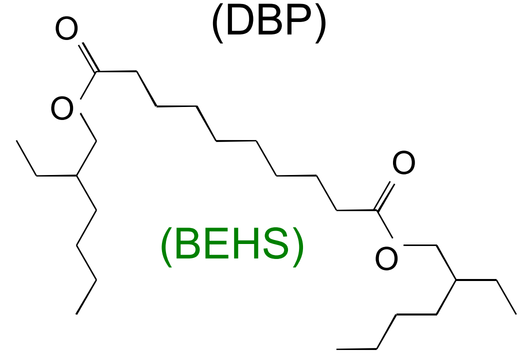


R45
M_n = 2,500 g/mole
~2.5 OH per chain

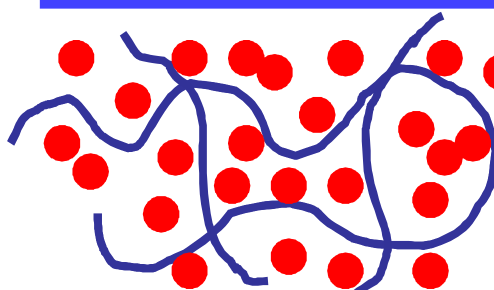
Primary solvents explored (DBP and BEHS)

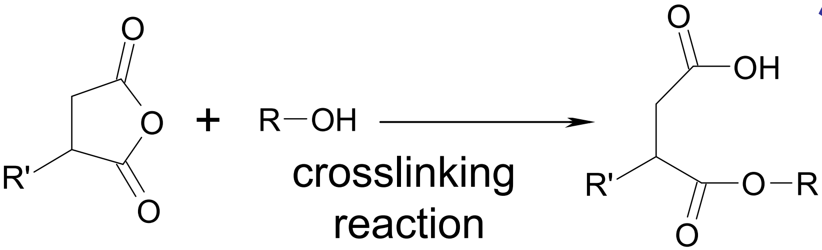


dibutylphthalate (DBP)

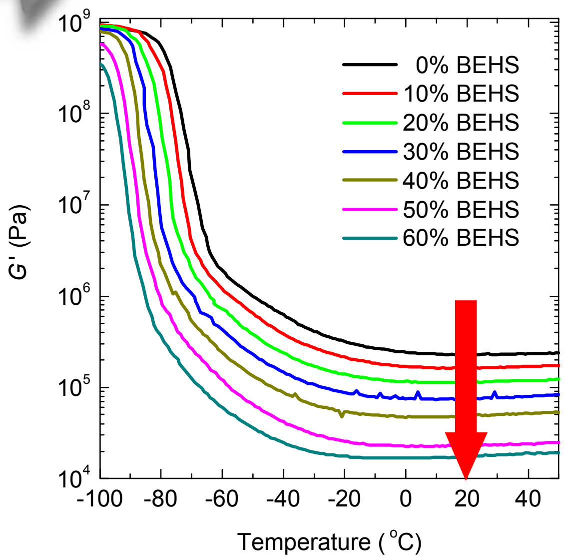


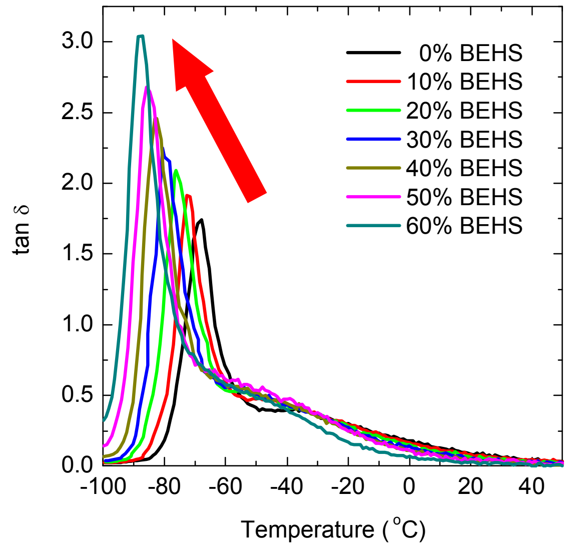
Crosslinked Polybutadiene swollen with solvent



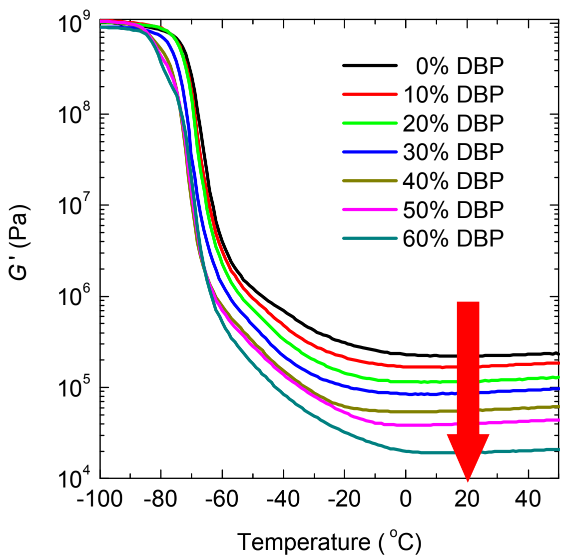


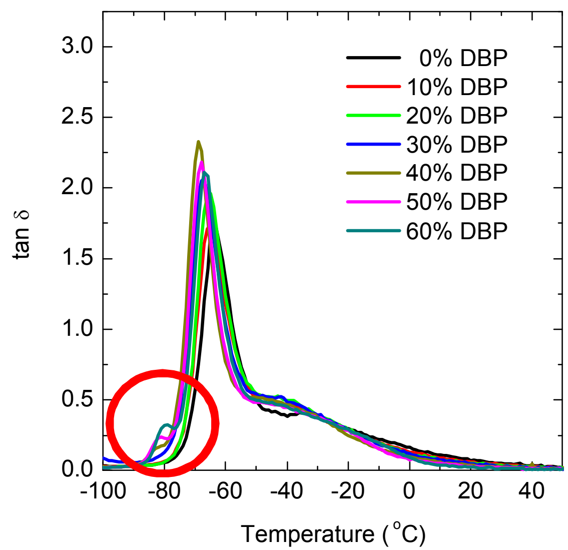
Solvent Impact on Mechanical Properties





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

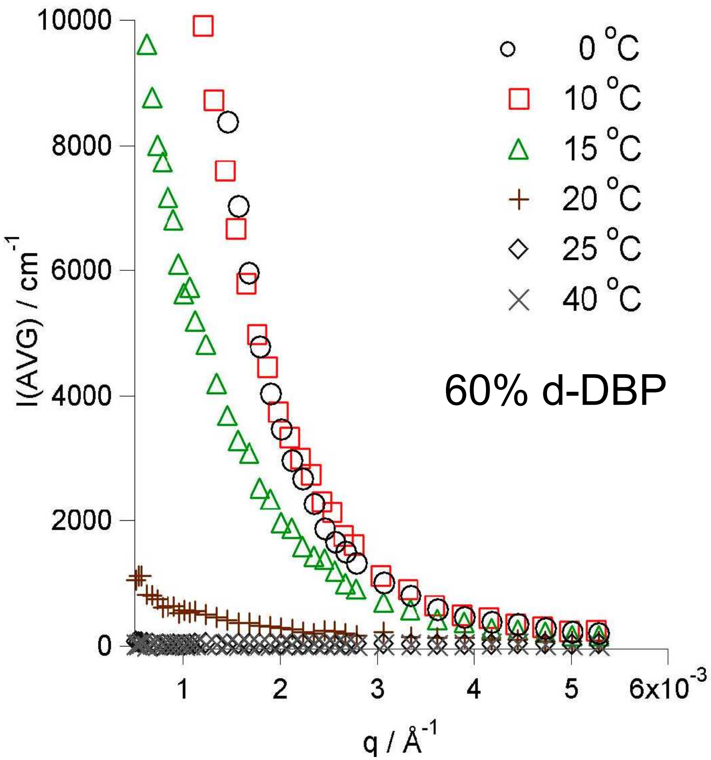


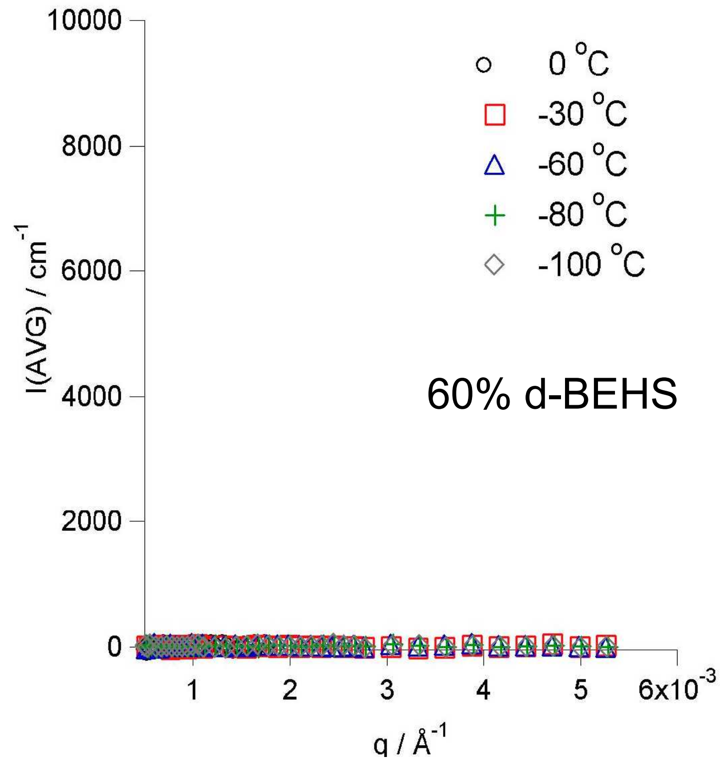


- Plateau modulus at T > -10 °C
- Modulus suppression with increasing solvent
- Phase separation with increasing DBP solvent
- Explains device failures

Neutron Scattering

Prof. Ronald Hedden
Penn State Univ.
Materials Science Dept

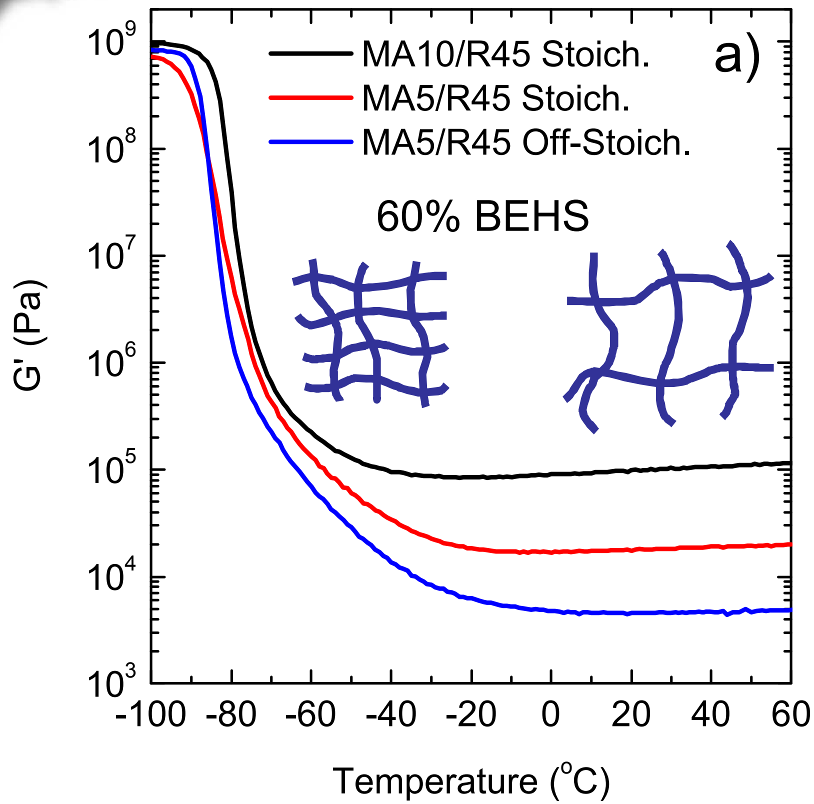


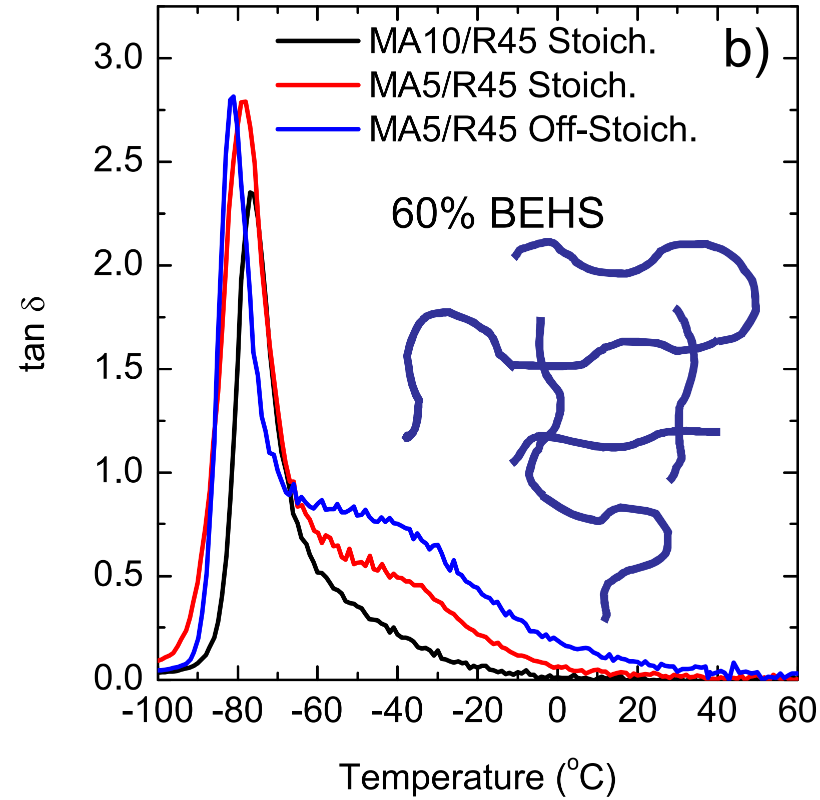


- Strong scattering temperature dependence
- 60% DBP phase separates below 20 °C
- 80% DBP phase separates below 60 °C
- DBP based gels performed poorly

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

Impact of Cross-link Density



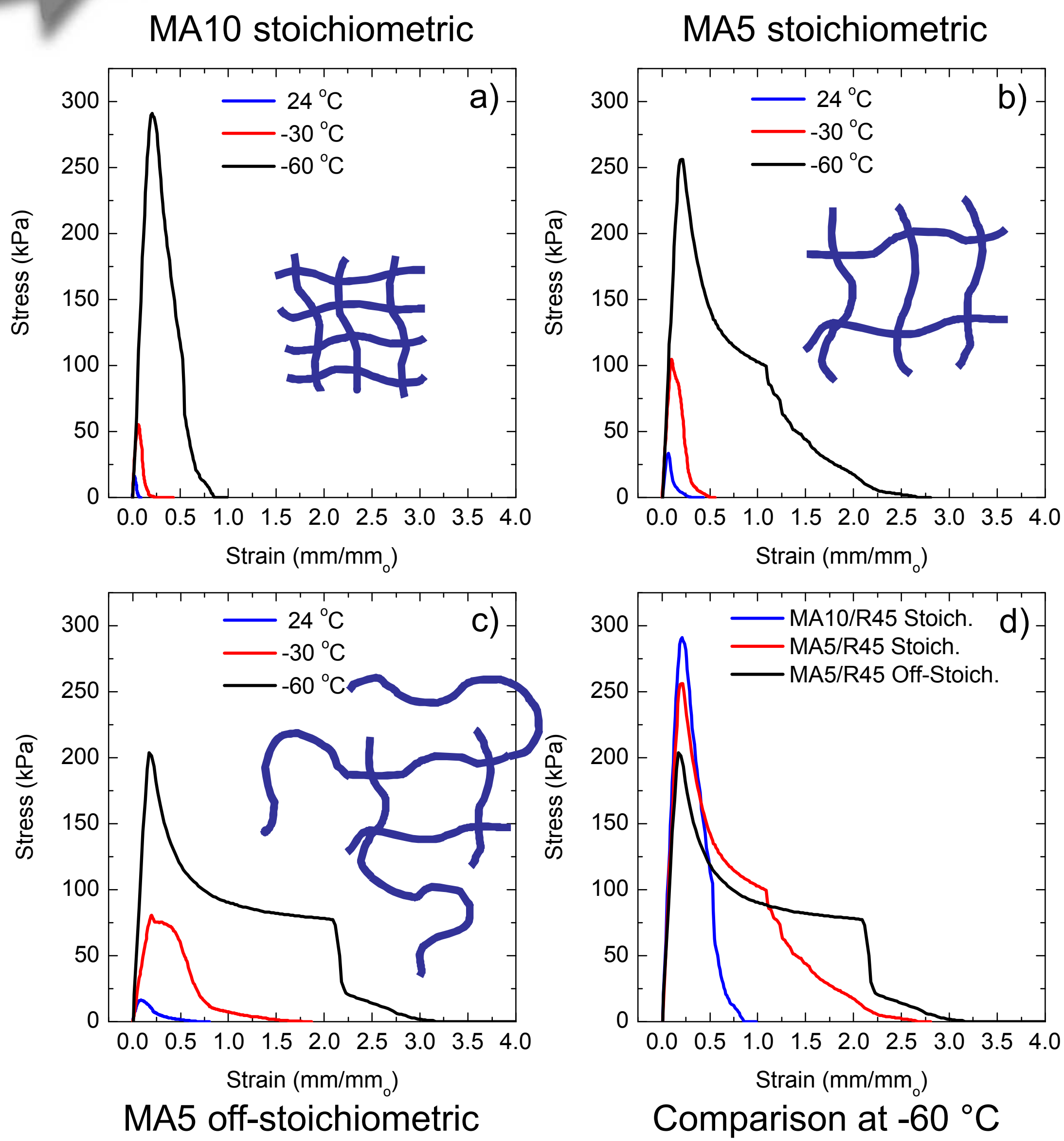


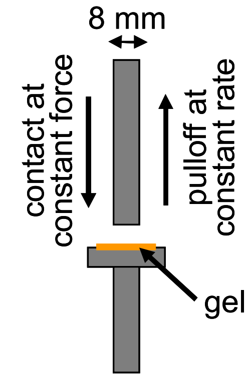
- Decreasing crosslink density decreases plateau value (reduced functionality, offstoichiometry)
- T_g identical
- Extractables equal at 61.5 ± 0.5%

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

Decreasing crosslink density and increasing defects improved performance

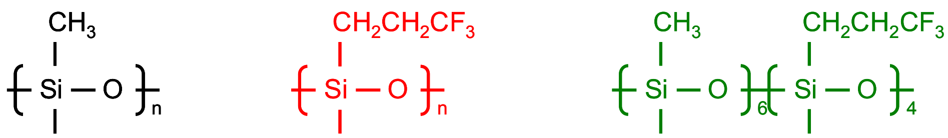
Correlation with Stress-Strain Diagrams



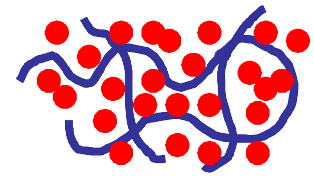


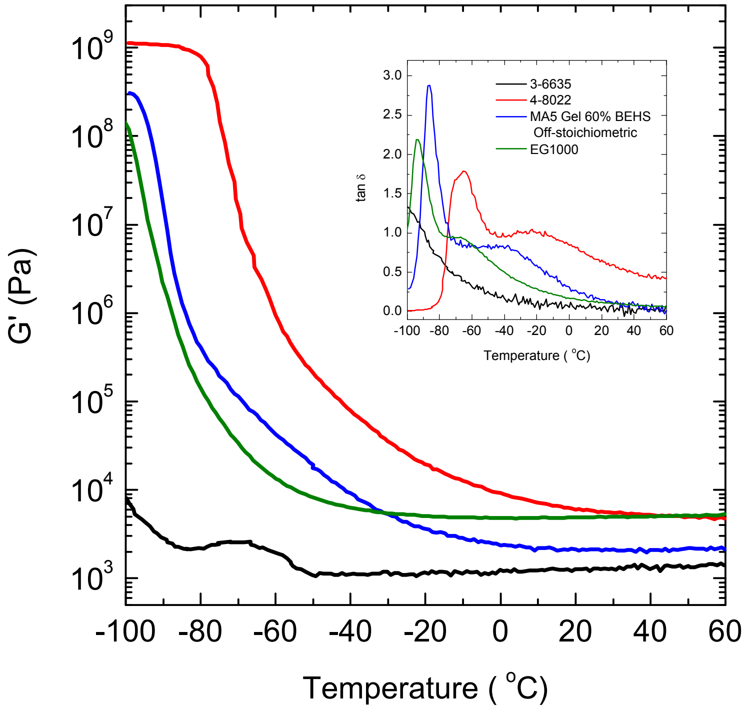
- As temperature decreases maximum and area increase (consistent with increasing loss tangent)
- As crosslink density decreases extension increases at all temperatures
- Gels with elastic tack behavior perform poorly
- Gels that exhibit extension and fibrillation in tack adhesion perform well

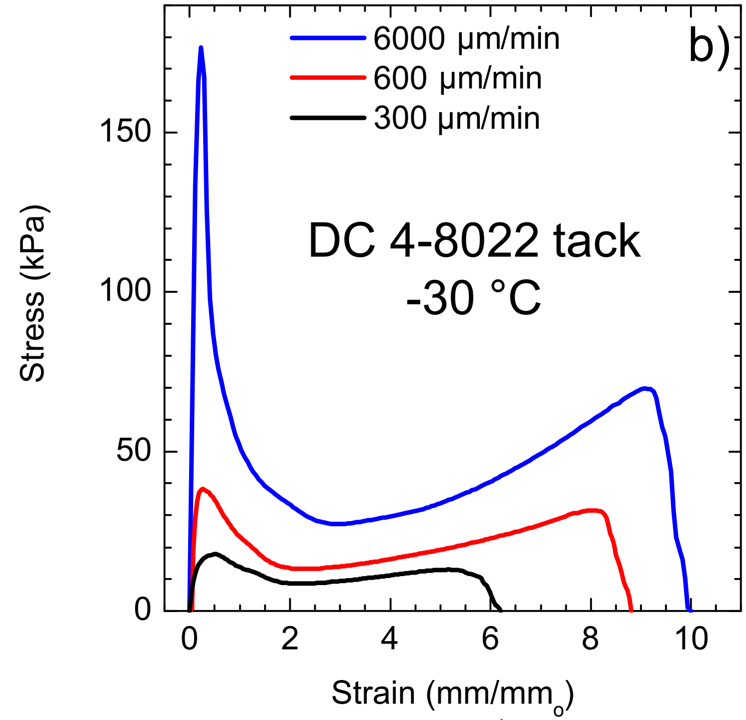
Transition to Silicones



DC 3-6635 DC 4-8022 EG 1000

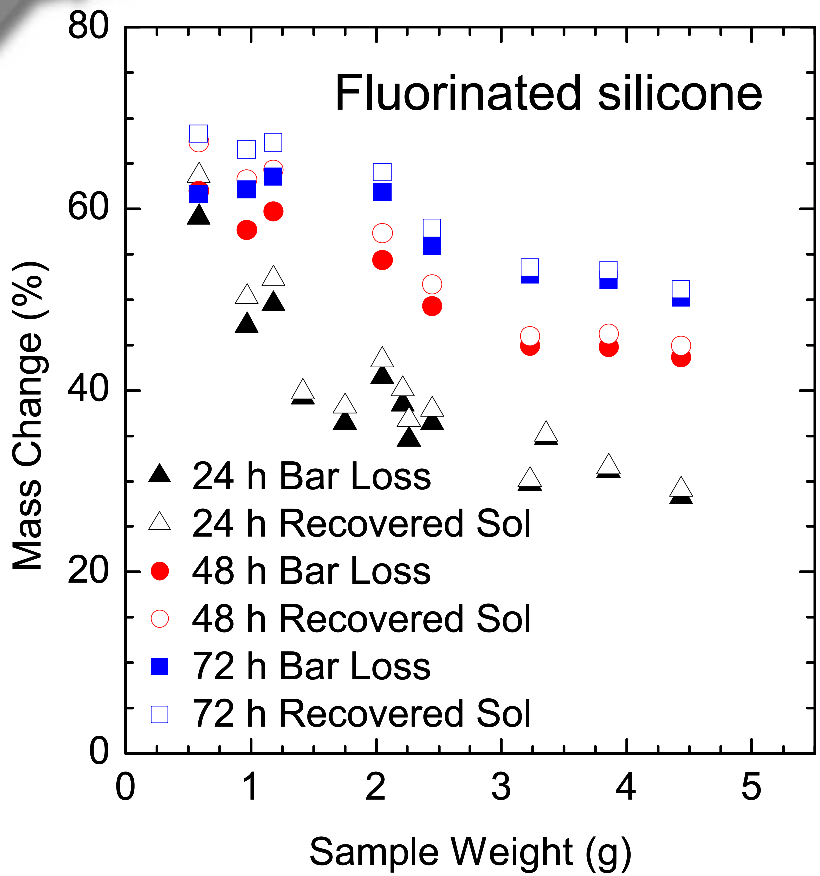




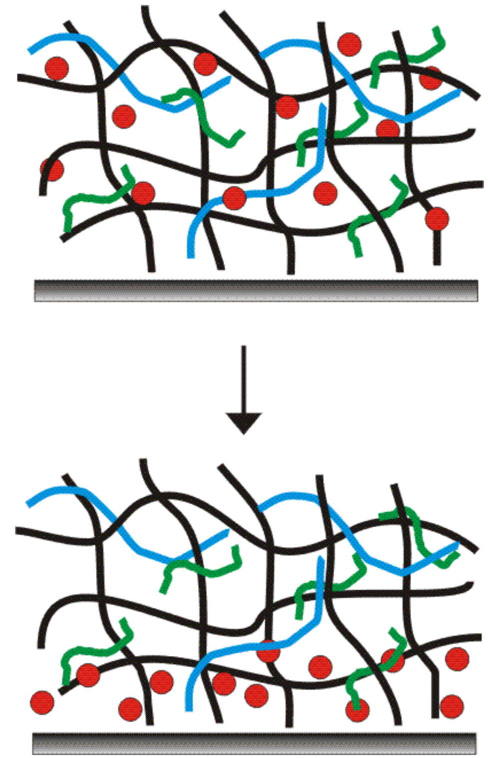


- Plateau value of G' for fluorosilicone and copolymer is less than 10^4 Pa
- High energy dissipation in loss tangent for both fluorosilicone and copolymer
- Rheology of fluorosilicone and copolymer similar to polybutadiene gel with BEHS
- Tack adhesion for fluorosilicone and copolymer exhibits extension and fibrillation
- Both fluorosilicone and copolymer perform well in devices
- Silicones are chemically stable with few aging mechanism in the temperature range

Extractable Sol Content in Silicones



potential sol aging mechanism



- Fully fluorinated silicone has ~ 65 mass% extractable sol
- Sol is high molecular weight based on time and sample size dependence for extraction

- Small molecule solvent-swollen polybutadiene gels exhibit rapid adhesive degradation upon phase separation
- Driving force: preference for small Mw polymer chains to adsorb at interfaces

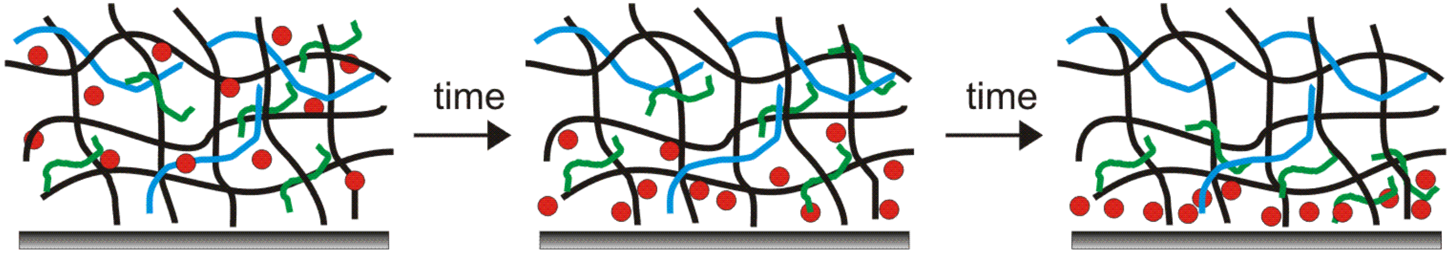
Does high extractables content represent a long term aging risk?
High Mw extractables means diffusion to critical interfaces is slow.

When is Sol an Aging Concern?

1. 30+ year lifetime requirements are stringent for most materials
2. Can sol migration towards interfaces degrade adhesion?
3. What is the kinetics of the sol diffusion?
4. How does this depend on sol size/branching and silicone Mc?

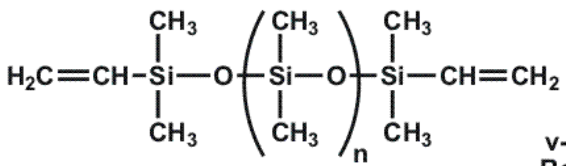
Dual Approach

1. Long-term aging study with intrinsic sol and 7 % additional oil
   - Peel adhesion, tack adhesion, torsional rheology, and extractable samples aged at 0, 24, 60, 75, 90, and 125 °C
   - Devices aged at 0, 24, and 75 °C
   - Testing at 18, 36, and 48 months
2. Model silicone system with controlled sol content
   - Impact of sol content, Mw, and gel crosslink density on adhesion, rheology, sol diffusion kinetics

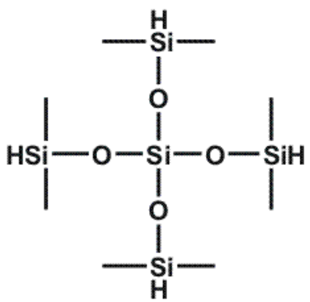


Model Silicone

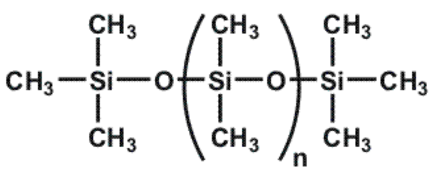
1. What sol fraction is optimal?
   - Too low – poor adhesion / mechanical properties
   - Too high – long term aging risk
2. How fast does sol migrate?
   - Mw/Mc dependence



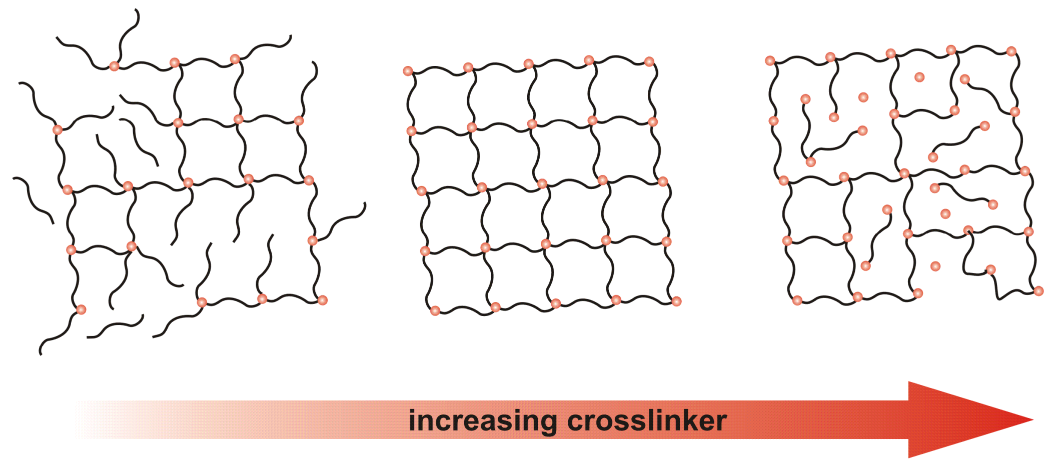
v-PDMS
Reactive
Vinyl Terminated PDMS



Tetrafunctional
Silane Crosslinker



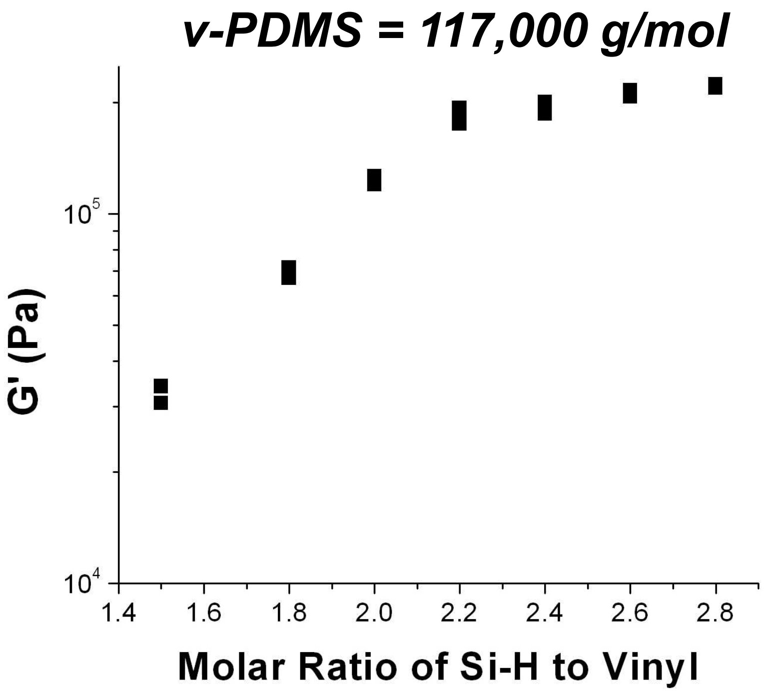
m-PDMS
Non-reactive
Methyl Terminated PDMS

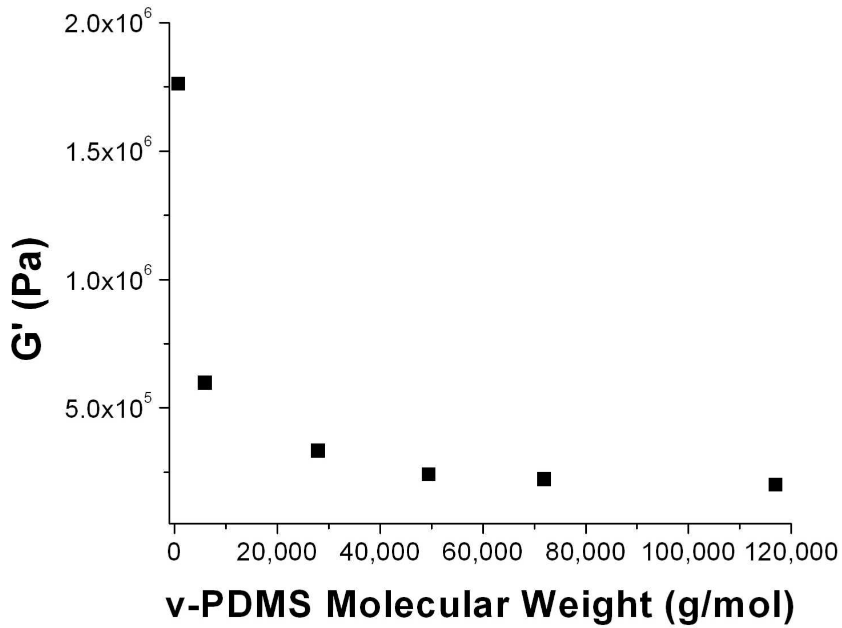


- Crosslink density controlled by v-PDMS molecular weight
- Molecular weight of v-PDMS and m-PDMS from 800 - 120,000 g/mol
- Different chemistry than fluorogel but sol-microstructure interactions should be similar

- Too little crosslinker
  - Large molecular weight unreacted sol
- Too much crosslinker
  - Large and small molecular weight unreacted sol
- Both cases decrease G'

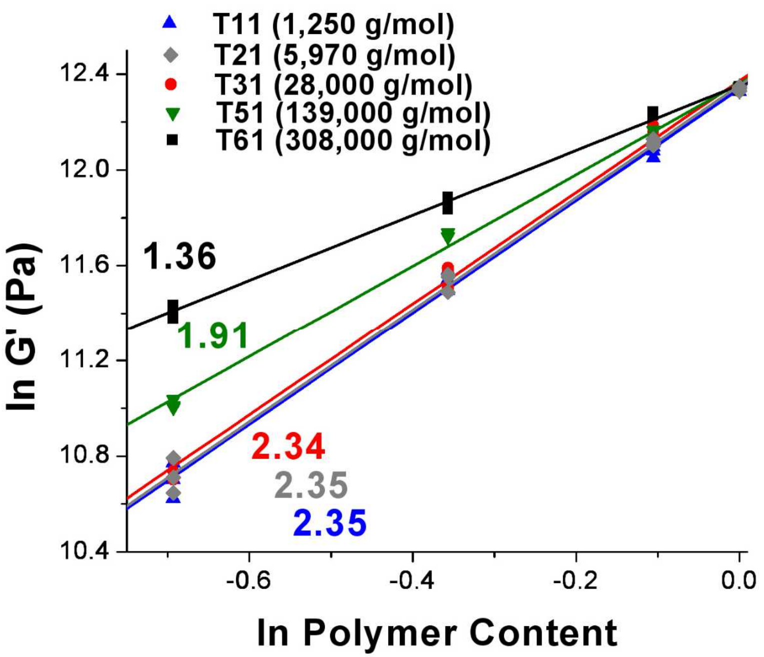
Optimum Stoichiometry

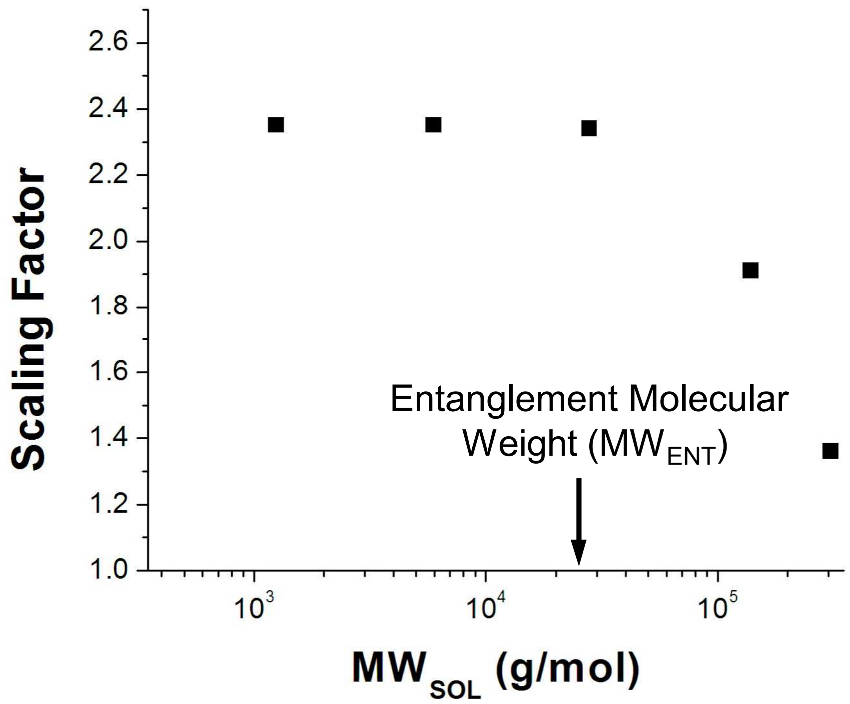




- Optimum ratio is not 1:1
- Plateau at high v-PDMS molecular weight due to entanglements dominating G' rather than the crosslinks
- Loaded networks with a range of m-PDMS molecular weight non-reactive sols

Effect of Sol Molecular Weight on Modulus

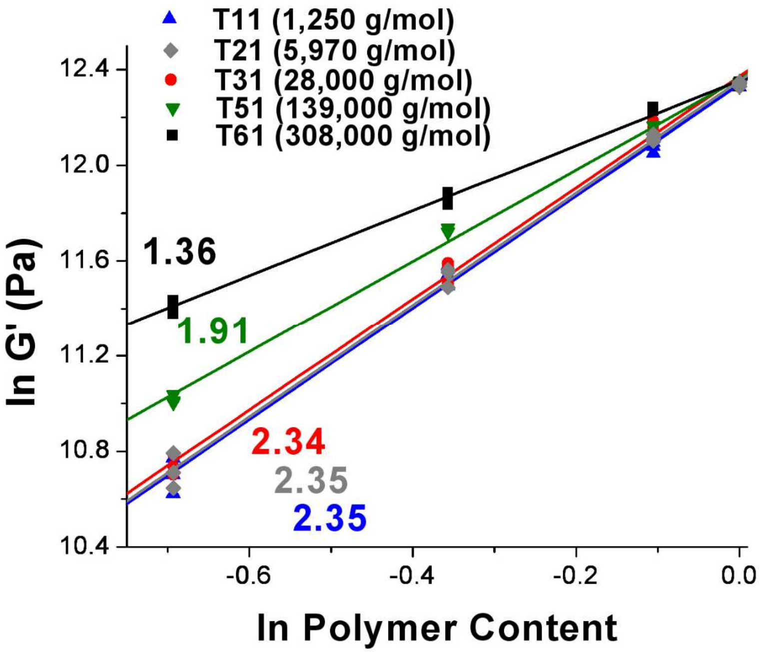


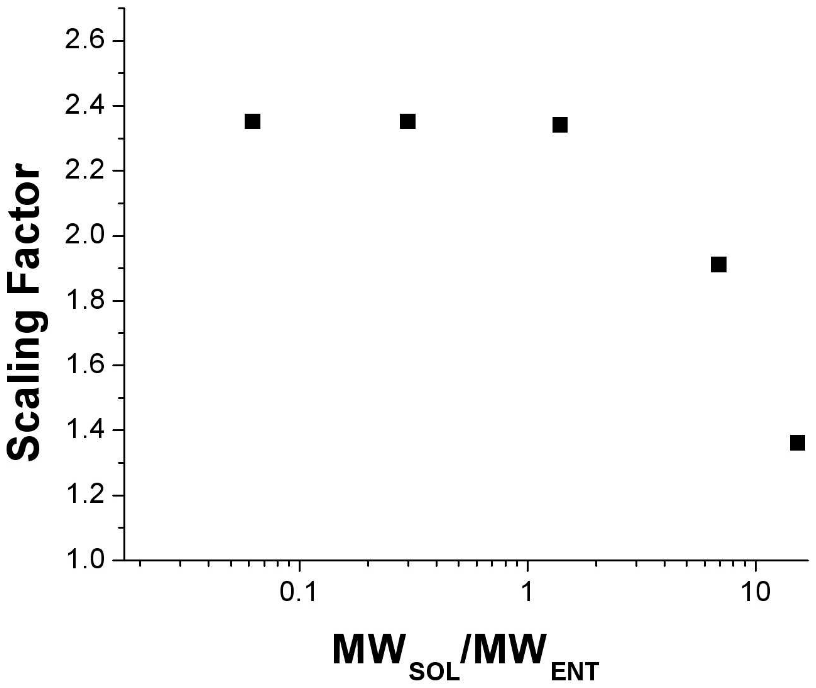


- Theoretical scaling factor of 2.3 for a small molecule theta solvent*
- Sol MWs ≤ MW_{ENT} exhibit similar scaling factors approaching 2.3
- Sol MWs > MW_{ENT} exhibit decreasing scaling factors
  - Sol can entangle with the network diminishing the change to the modulus

* Sivasailam and Cohen, *J. Rheol.* **2000**, *44*, 897

Effect of Sol Molecular Weight on Modulus





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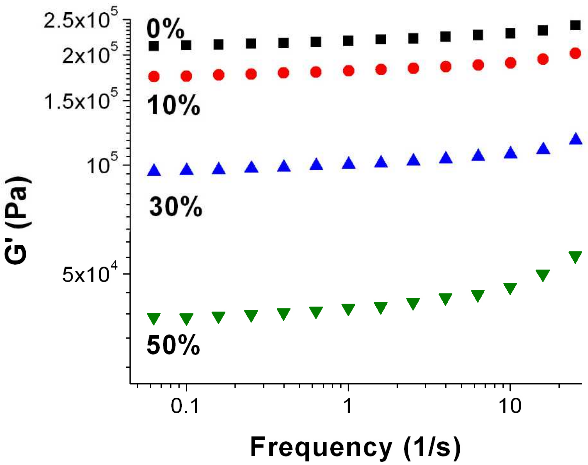
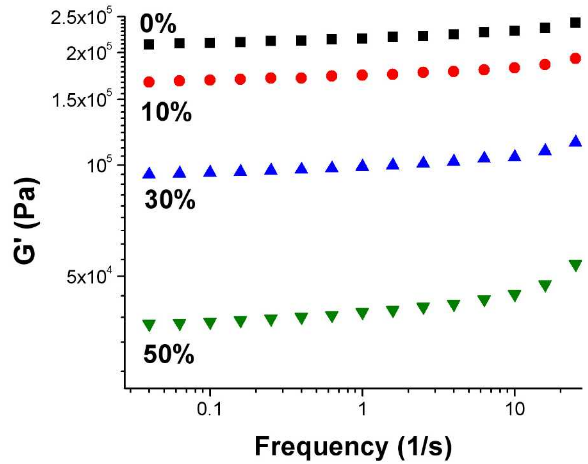
Frequency Dependence

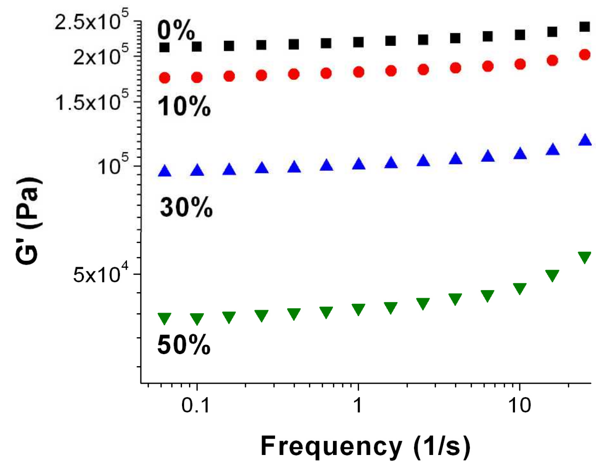
T11



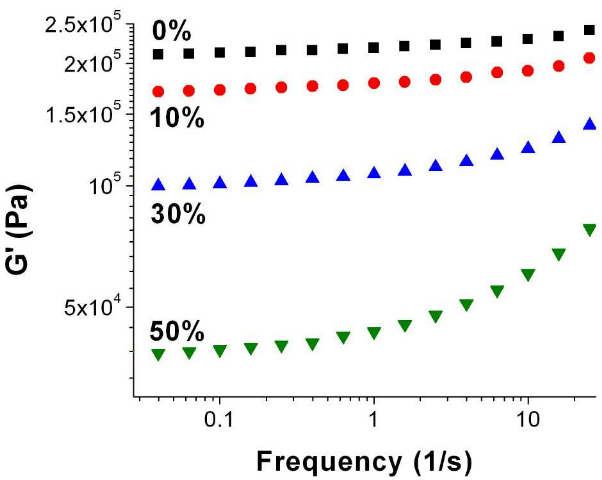
T21



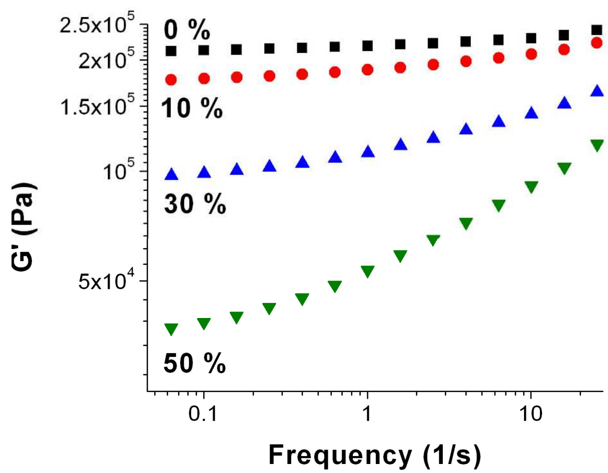
T31



T51

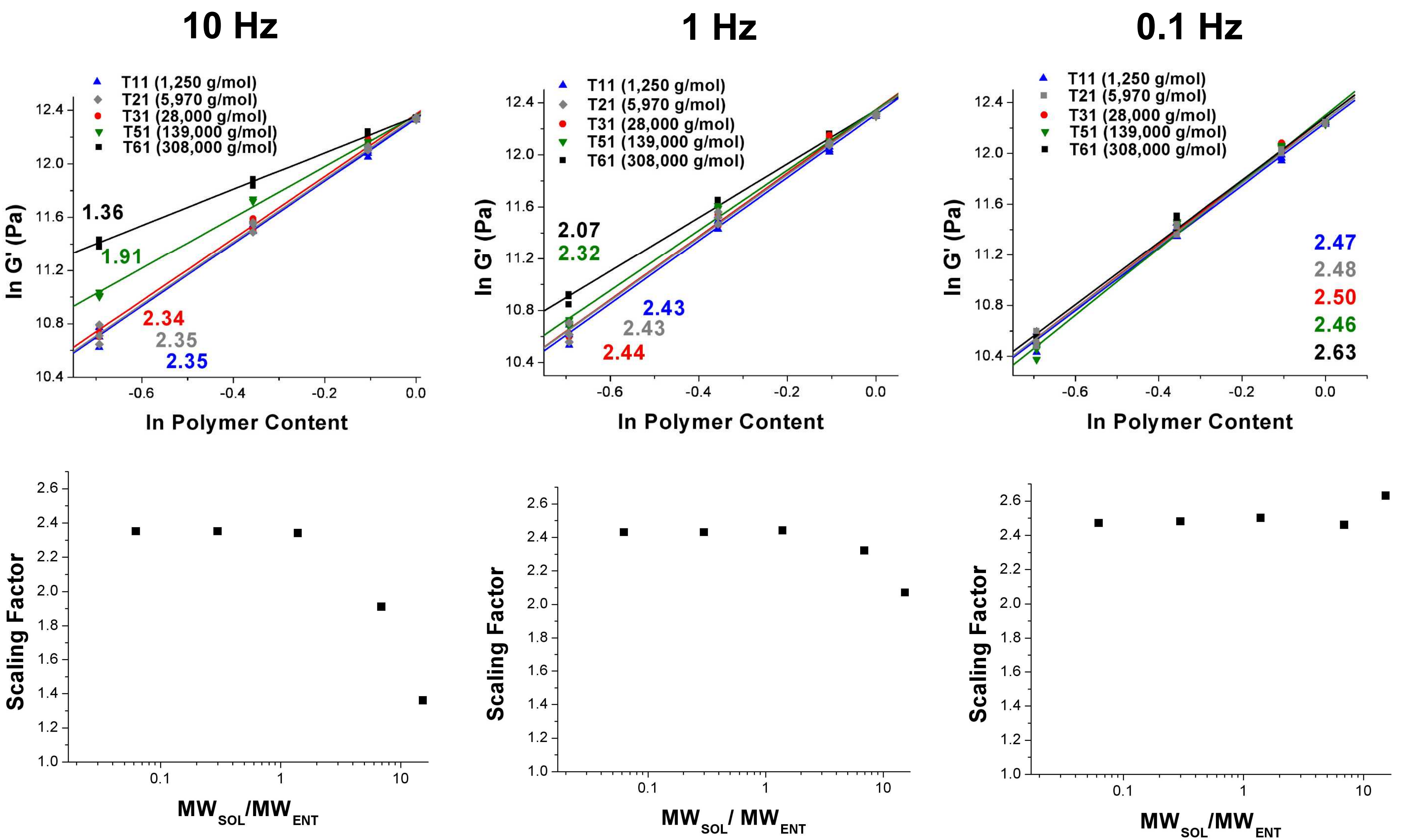


T61

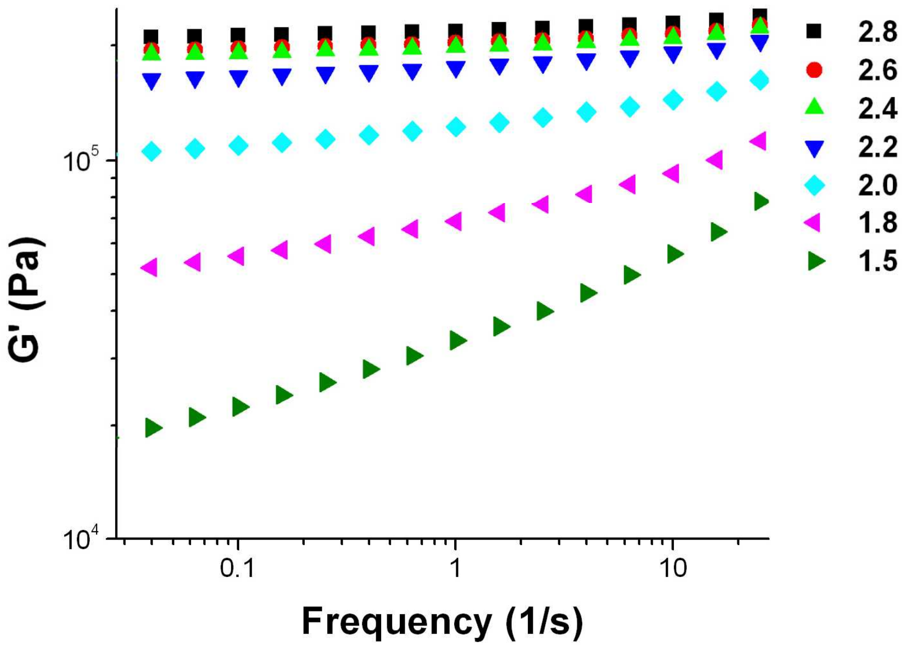


- Sol MW > MW_{ENT} has a significant frequency dependence
- Frequency dependence may indicate a change in the mobility of the solvent or a change in the network microstructure
  - Larger MW sol require longer times to migrate

Frequency Dependence of Scaling Factors



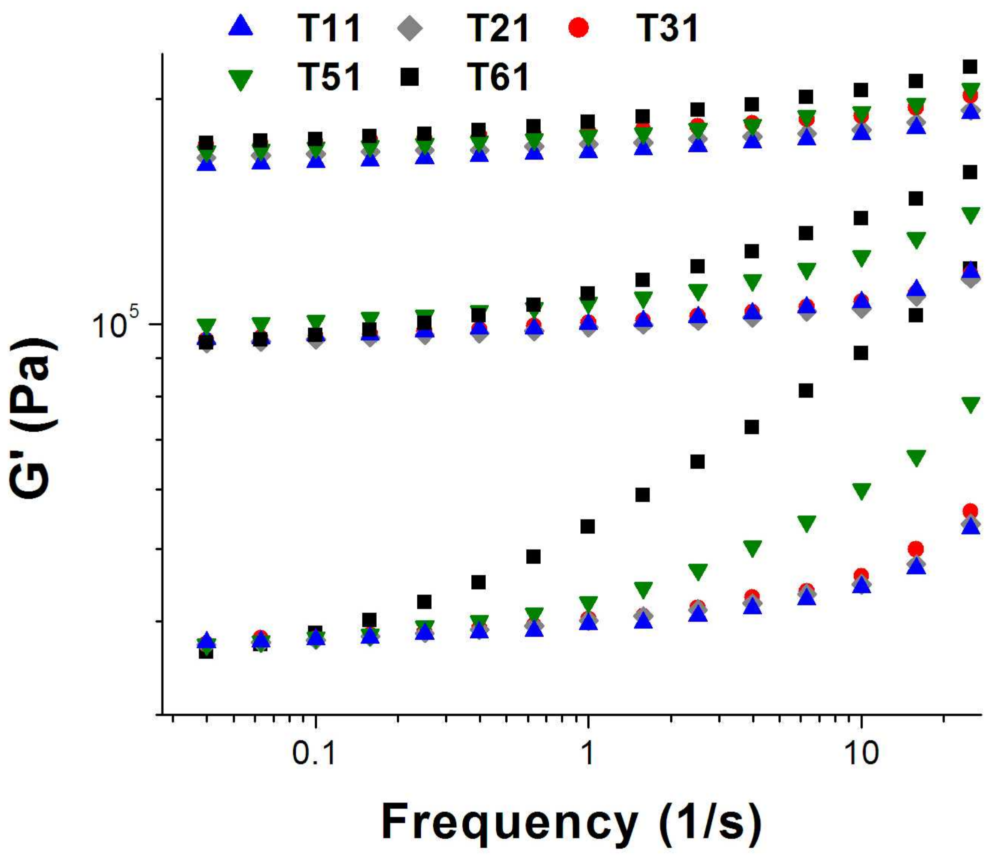
Frequency Dependence of Imperfect Networks



- Networks formed with non-optimized stoichiometry exhibit a frequency dependence
  - Attributed to the mobility of the dangling chain ends

- For 50g of this v-PDMS the difference of 0.1 in the molar ratio is equivalent to 8 μL of SiH

Frequency Dependence



- Overlays of loaded gels exhibit overlap at low frequencies
  - Indicating a consistent network microstructure

Summary/Future Work

- Insight into the aging mechanism is critical when developing a materials solutions
- Silicone gels were developed that met all performance requirements and had less aging risk than solvent-swollen gels
- A model silicone system is being investigated to understand role of sol content and molecular weight on initial gel properties and potential for gel aging.
  - Initial results indicate that high molecular weight sols have a lower scaling factor and exhibit a frequency dependence
- Further experiments are planned to correlate the frequency dependence with the solvent mobility by coupling with tear testing, swelling/deswelling, and sol labeling and expanding the study to additional crosslink densities and sol MW.
- Extract solvent and retest scaling factors to gain insight into the network structure
- Determine an optimum sol fraction and molecular weight for a polymer network with a given crosslink density to provide good adhesive and mechanical performance while minimizing long-term degradation

Acknowledgements

1821
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