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Rheology and Adhesion of Lightly Cross-linked Polymer Gels

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Engineering Sciences

Sandia National Laboratories

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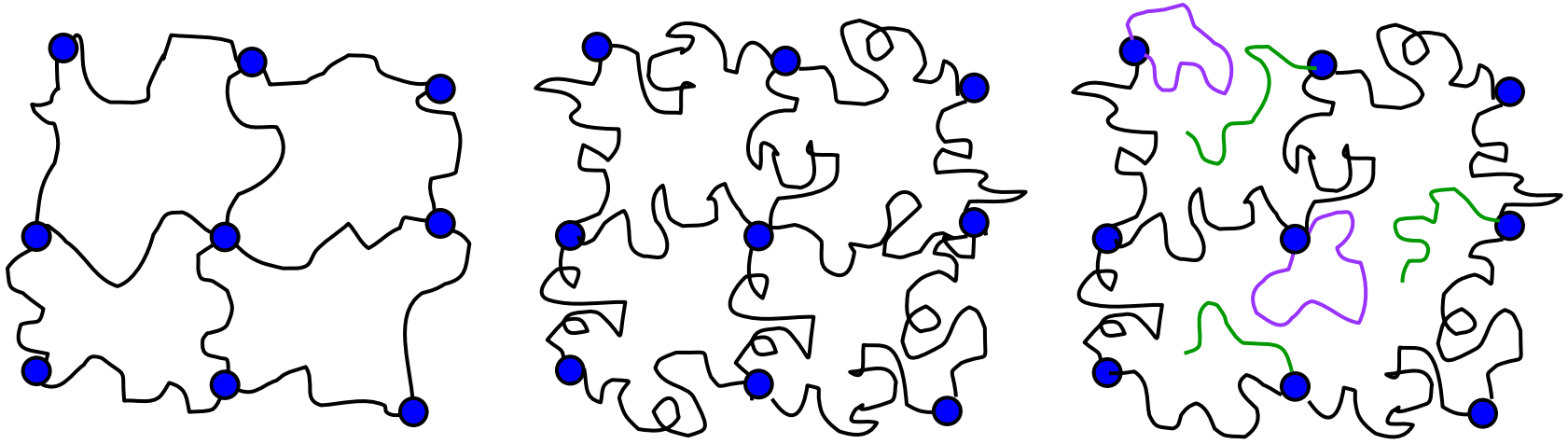
Polymer Gels

- Lightly Crosslinked Polymer Gel
  - Viscoelastic solid
  - Equilibrium Modulus
- Polymer Gels Make Good Adhesives
  - Stay where they are placed
  - Large work of adhesion
  - Tailor properties to release from surfaces

Polymer Gels

- Dow Corning DC 4-8022
  - Soft fluorosilicone gel with extractables content of ~55%
  - Non-ideal gels
    - Defects
    - Entanglements
    - Diluted with entangled polymer

	G' [Pa] (0.01Hz)
High	1060
Medium	471
Med-Low	229
Low	157



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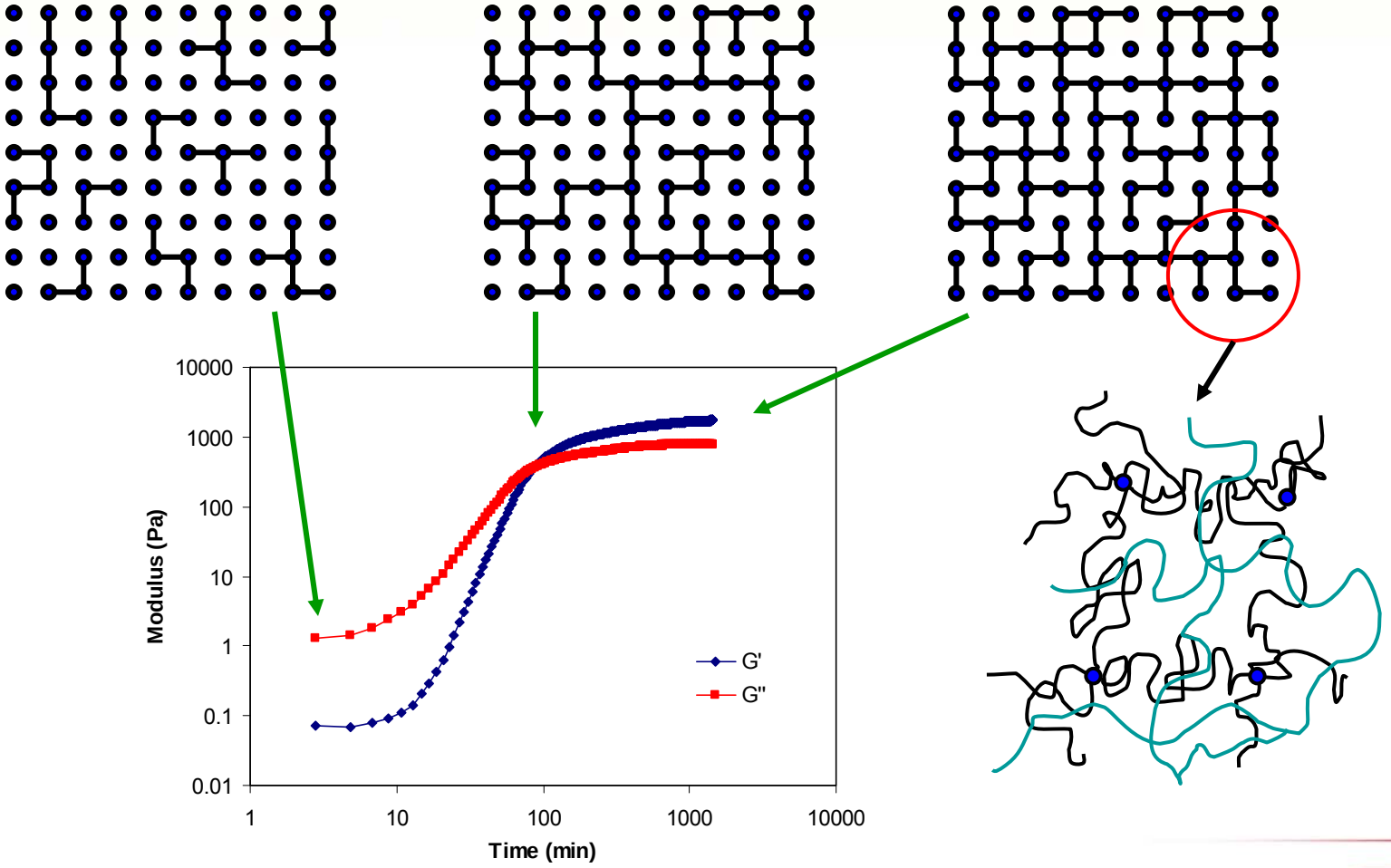
Gelation

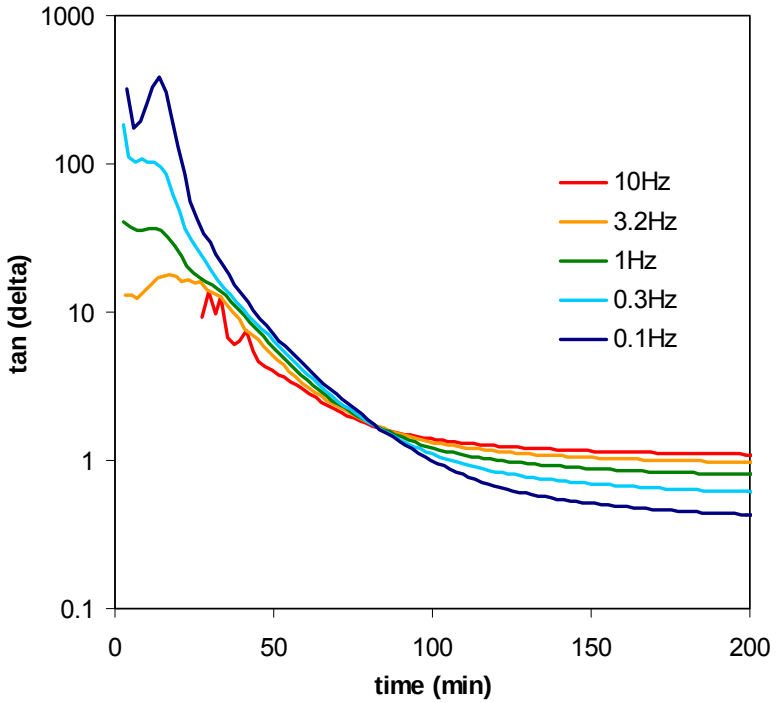
- Gelation with a chemical crosslinking reaction



Larson (1999)

Critical Gel Point

- Critical gel point – Chambon & Winter (1987)
- Softer gels have more defects



$$G', G'' \propto \omega^n$$

$$\frac{G''}{G'} = \tan(\delta) = \tan\left(\frac{n\pi}{2}\right)$$

	n
Ideal	**0.5**
High	**0.61**
Medium	**0.66**
Low	**0.7**

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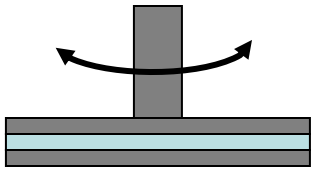
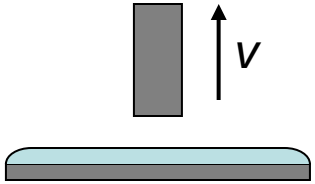
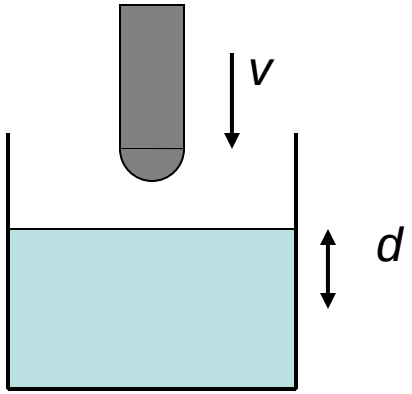
Time Scales in Rheology & Adhesion

- Linear Oscillatory Rheology
- Tack Adhesion
- Hardness

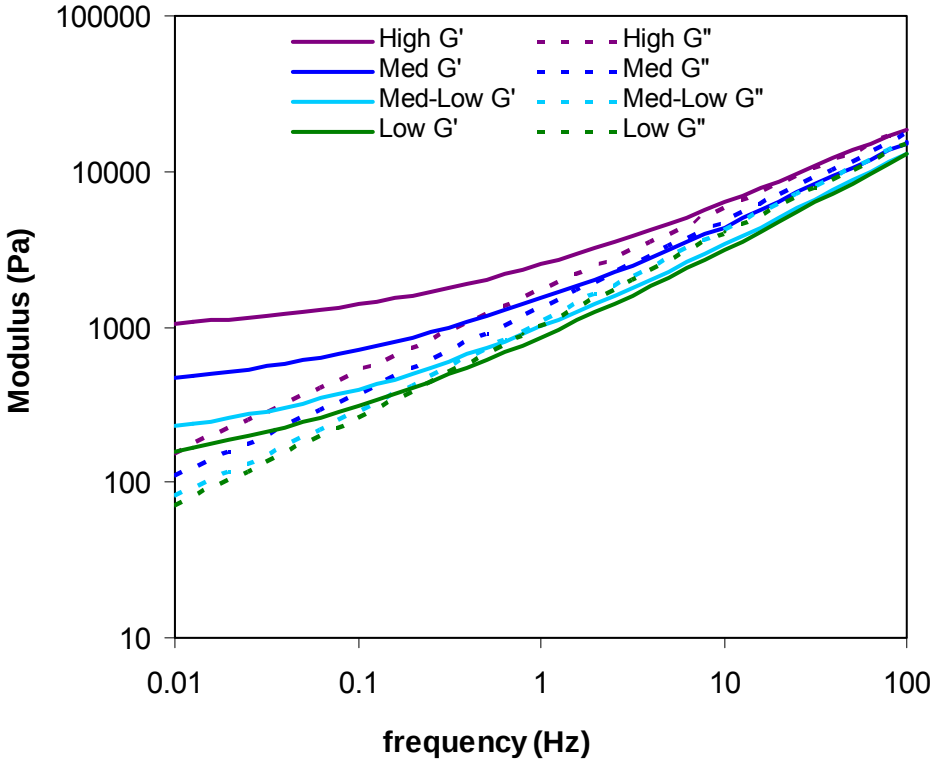


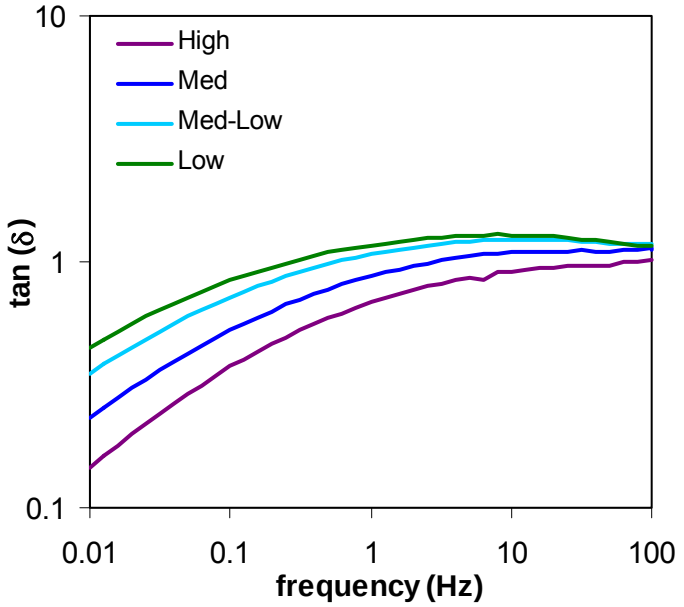




Oscillatory Rheology

- At low frequencies, elastic modulus G' dominates viscous modulus G" and approaches a plateau value equilibrium modulus G_{eq}
- At high frequencies, dissipation due to physical entanglements and internal friction become important





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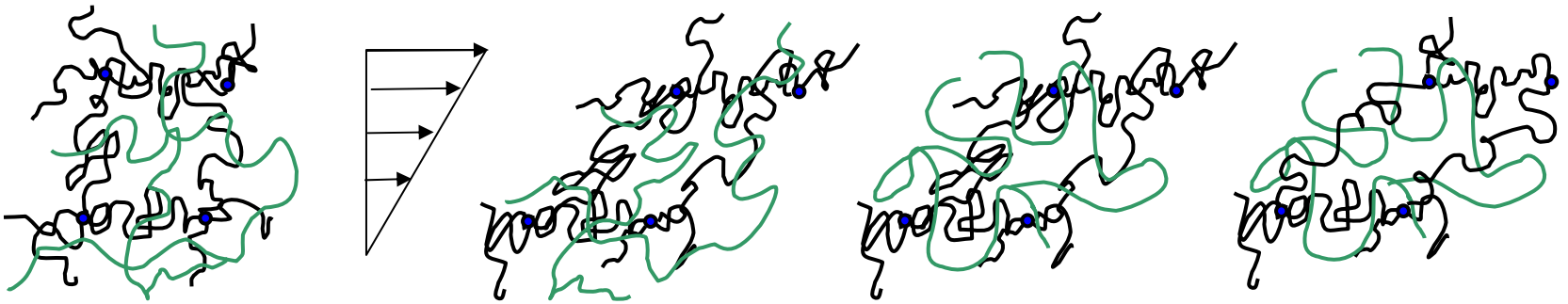
Relaxation Dynamics

- Lightly crosslinked polymer gels have a wide range of relaxation dynamics



$t = 0$
All polymers are stretched and aligned storing elastic energy

$t > \lambda_{sol}$
Free polymers relax, releasing entanglements & stress

$t > \lambda_{gel}$
Gel polymers relax releasing more stress

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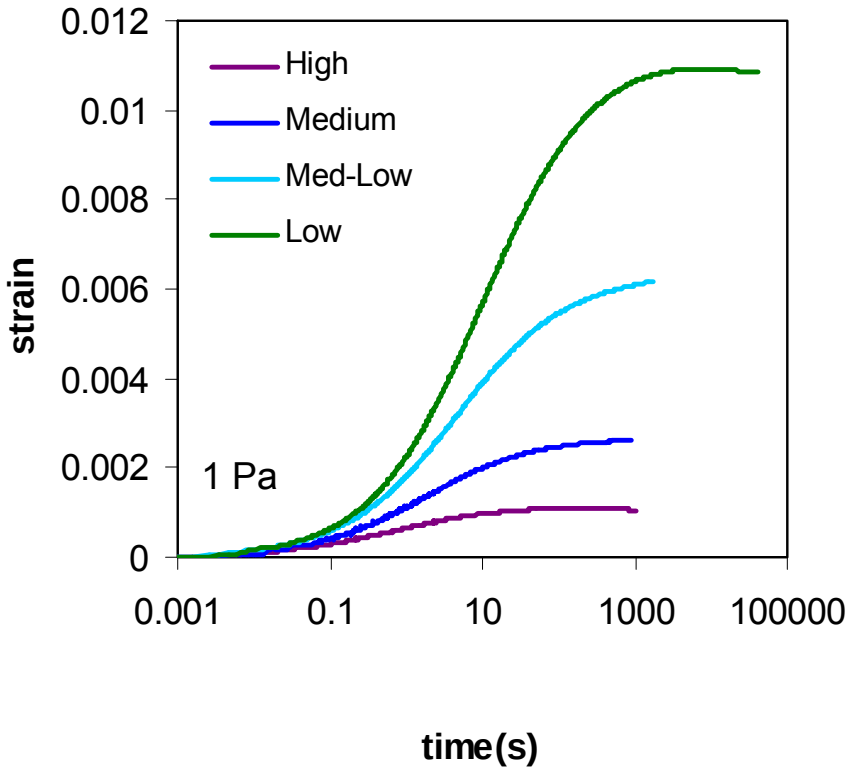
Creep of Polymer Gel

- Slow relaxation dynamics are apparent in creep experiments



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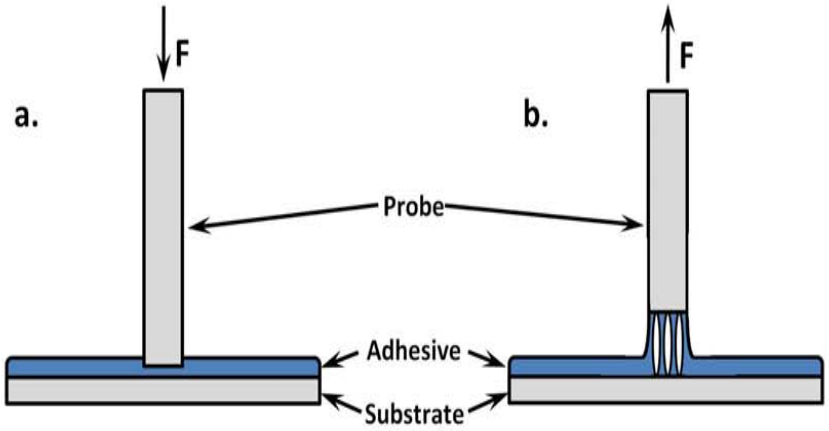
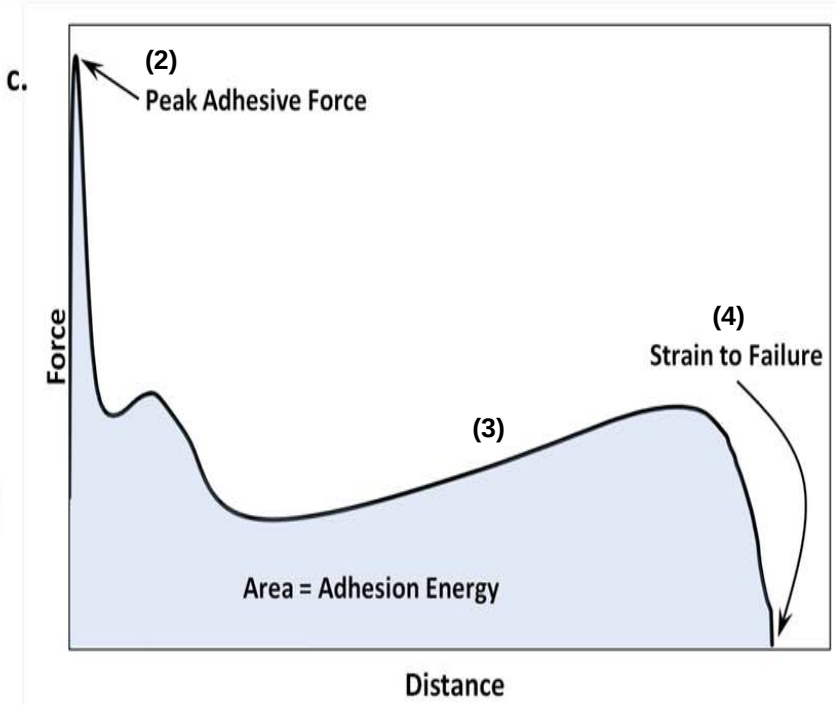
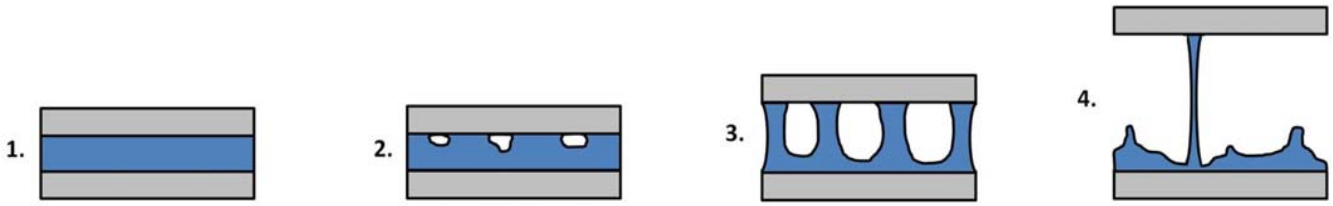
Tack Adhesion Measurements







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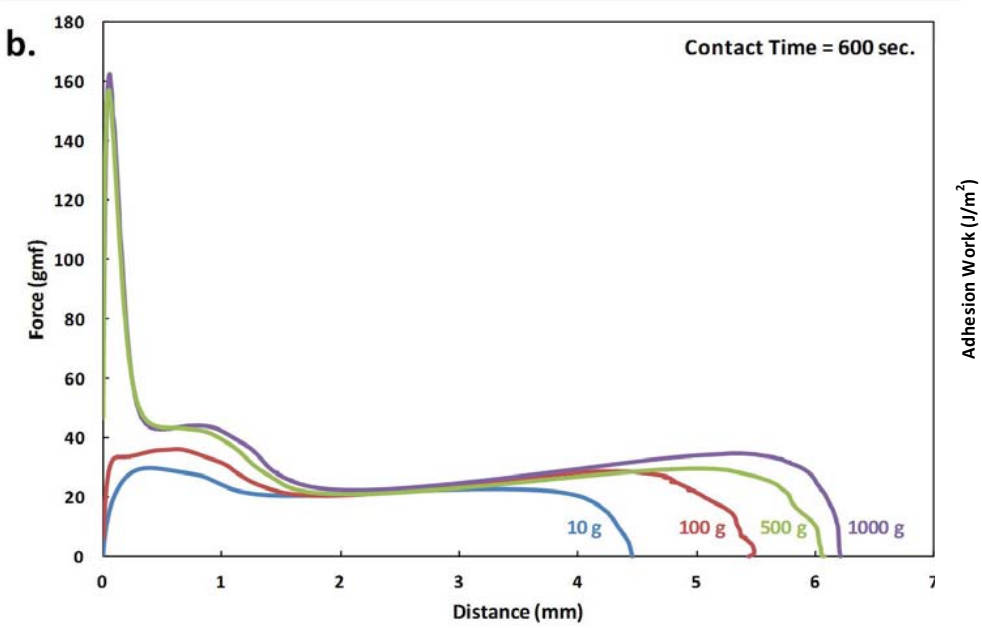
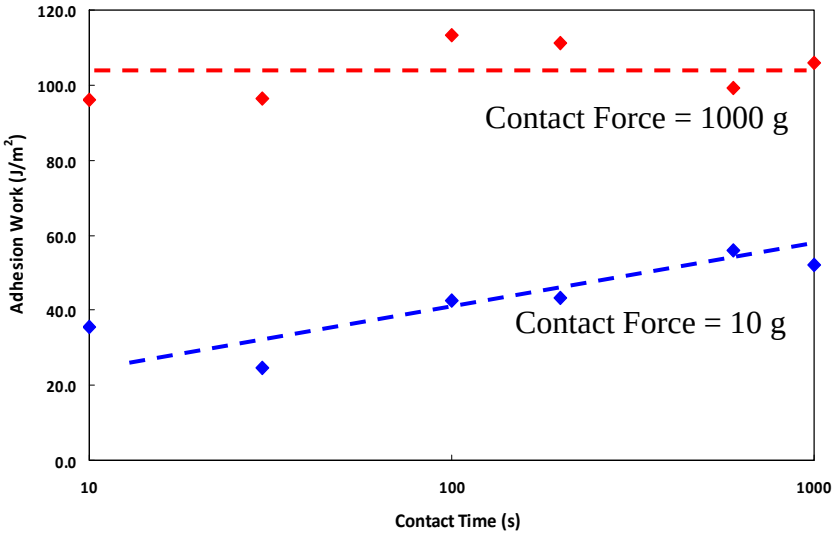
Adhesion depends on contact

- Larger contact force and time improve work of adhesion
  - Enable intimate contact between gel and probe





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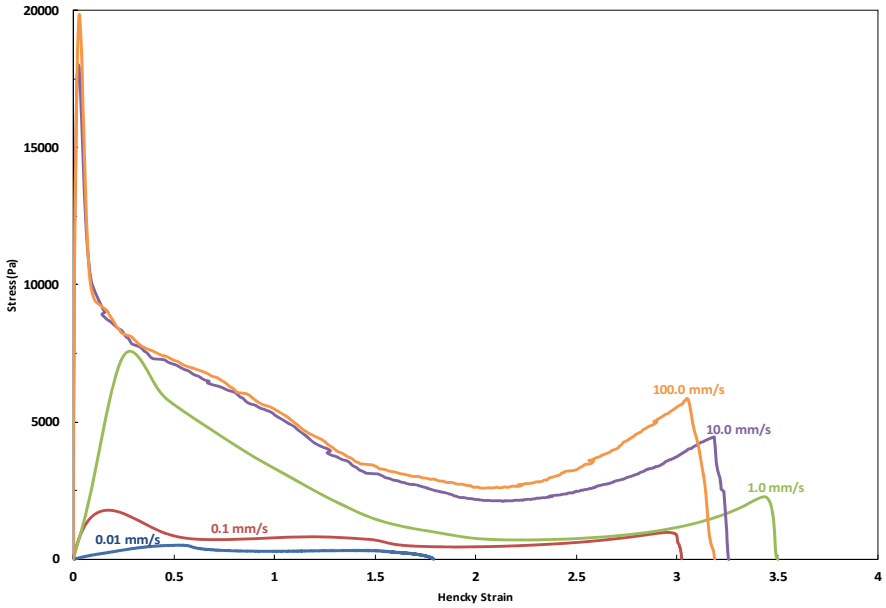
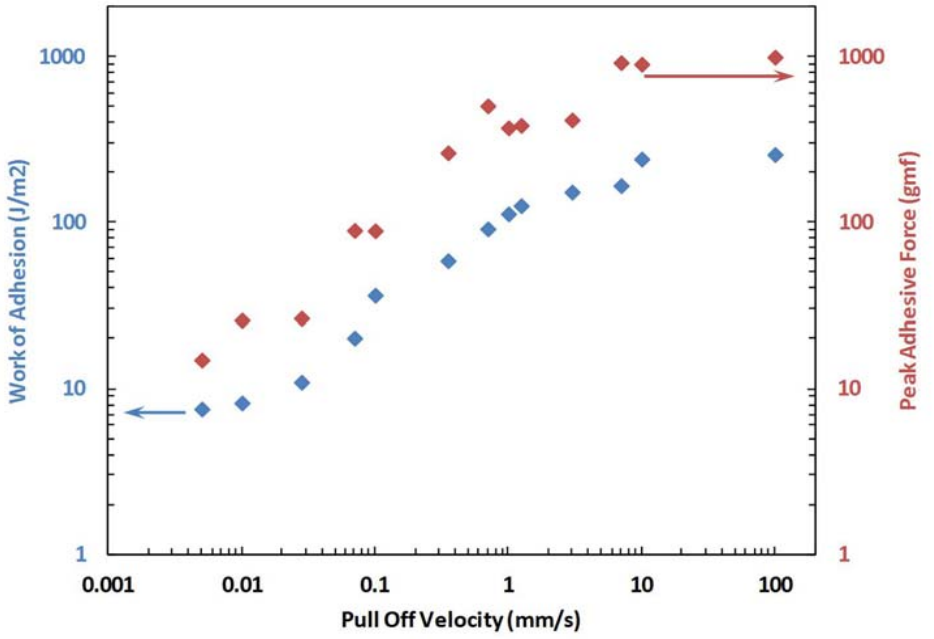
Speed Dependence of Tack

- As pull off speed increases, peak adhesive force and work of adhesion increase





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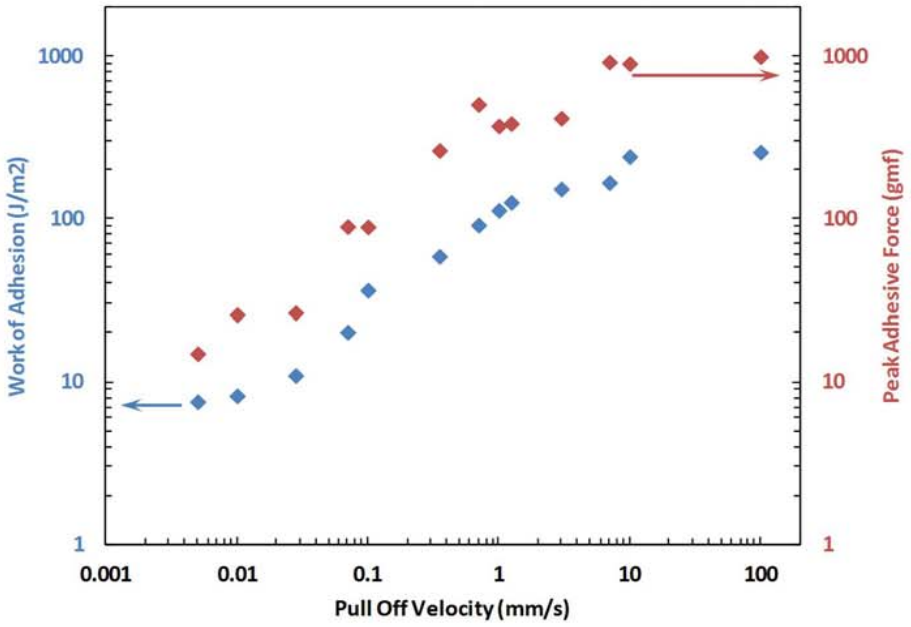
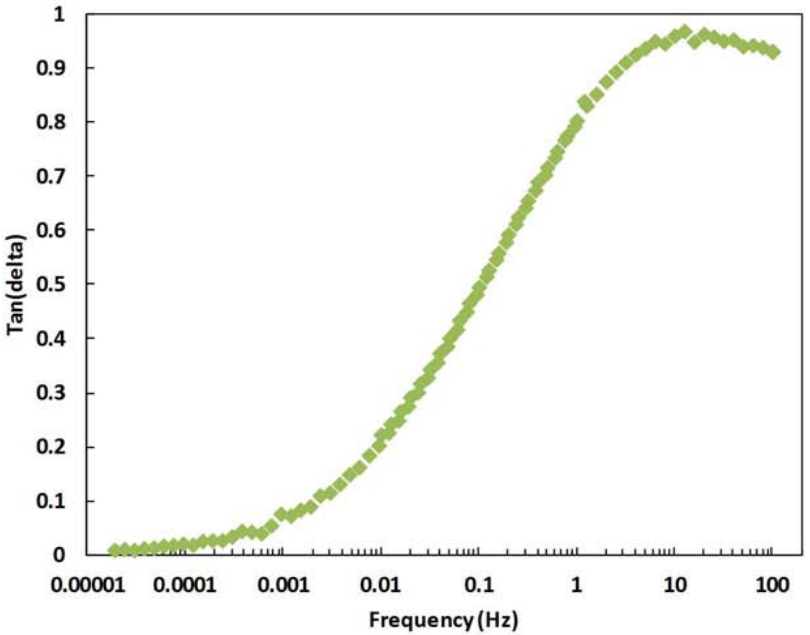
Relaxation Dynamics in Gel

- At faster speeds, increases in work of adhesion and peak pull-off force are linked to increase in viscous effects in polymer gel





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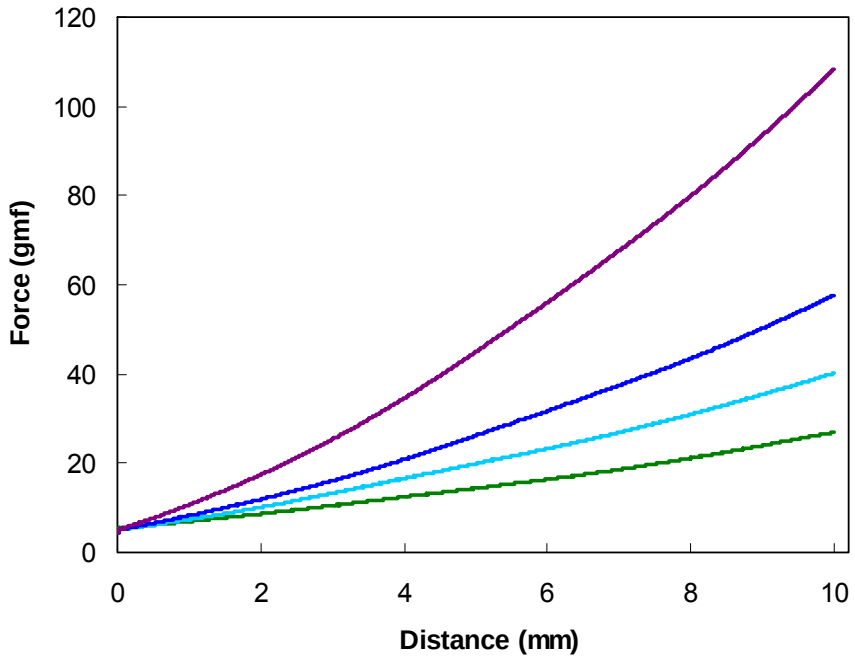
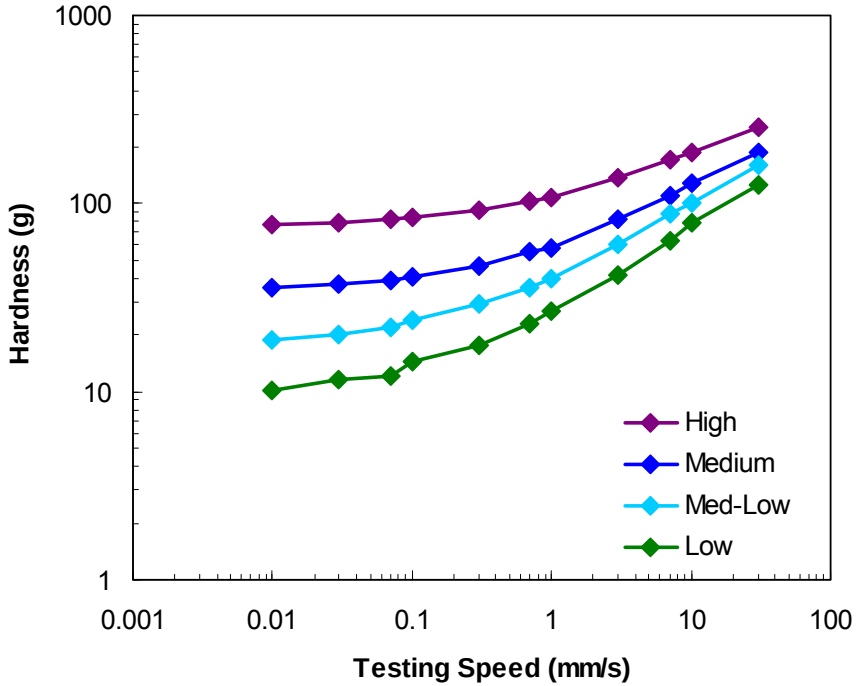
Hardness of Polymer Gels

- Indentation of polymers used to measure hardness
- Also observe speed dependence in measured hardness





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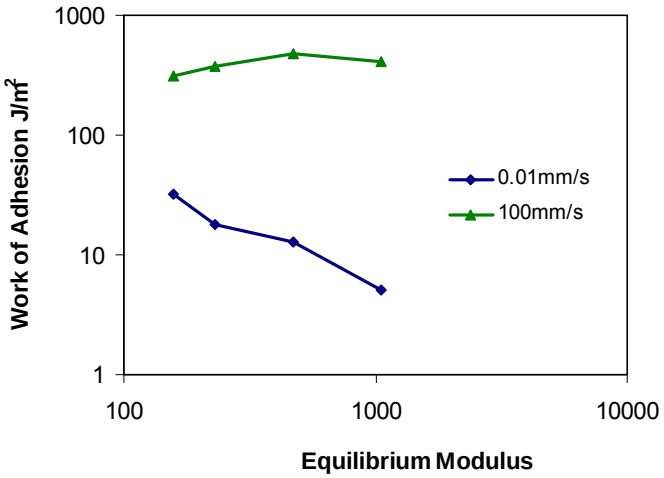
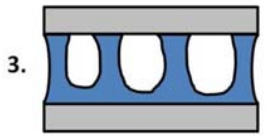
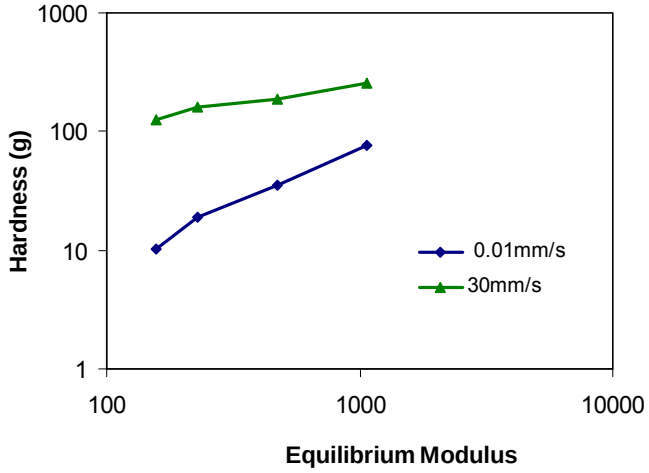
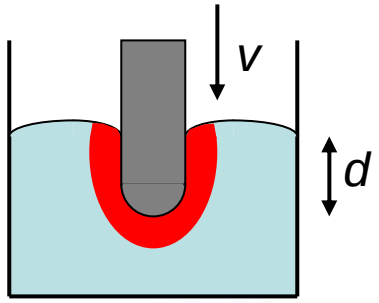
Dependence on G_{eq}

- Only observe strong dependence on equilibrium modulus G_{eq} at slow speeds









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Summary

- Lightly cross-linked polymers have a broad spectrum of relaxation dynamics which affect all forms of characterization
- Linear Oscillatory Rheology shows
  - Equilibrium modulus at low frequencies
  - Frequency dependence at high frequencies
- Adhesion is time-dependent
  - Poor adhesion at slow pull-off speeds related to relaxation time of dissipative modes in gel
- Hardness is correlated to rheology and adhesion, but complicated non-uniform strain