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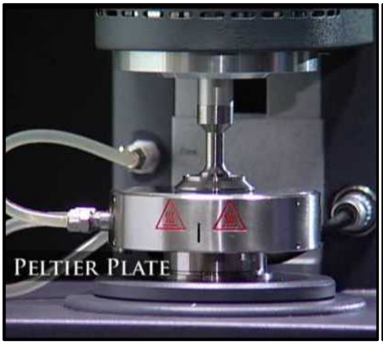

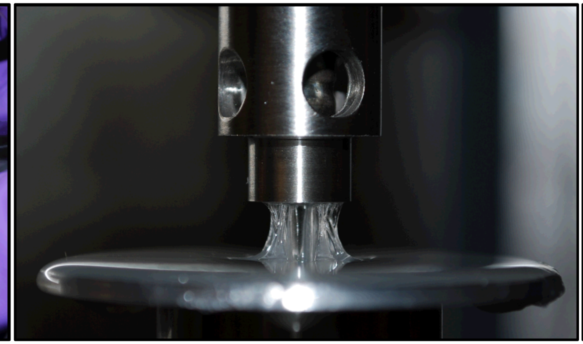

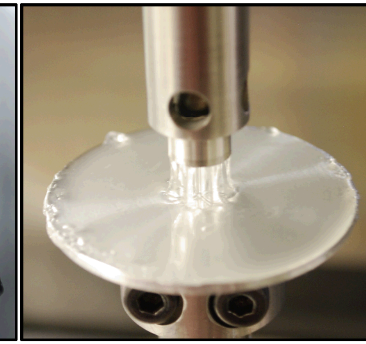

Rheology, Adhesion, and Debonding of Lightly Cross-linked Polymer Gels

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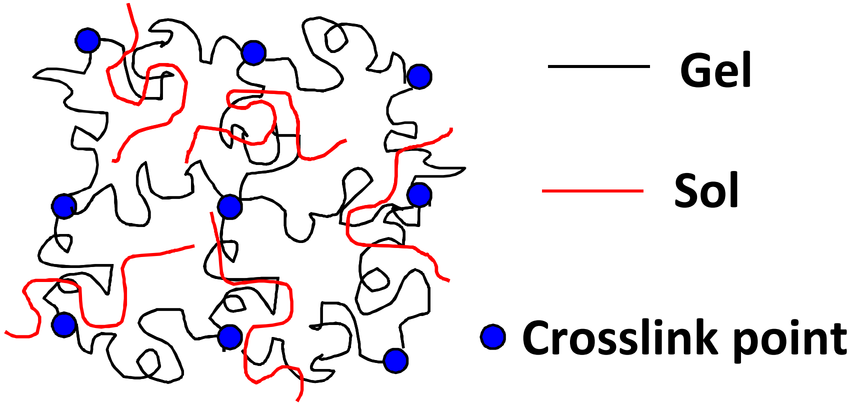
Polymer Gels

- **Polymer gel** – physically or chemically **cross-linked** network of polymers which is swollen by a liquid
- **Network** structure formed by polymer chains that are physically (entanglements) or chemically (covalent bonds) bound together
- **Sol** is the fluid that dilutes or swells the polymer network
  - Can be a simple fluid (e.g. Newtonian small molecule solvent like water or acetone)
  - Can also be a complex fluid (e.g., entangled polymer solution)
  - Nature of the sol significantly contributes to and determines the overall material response

Chemically Cross-linked Gel



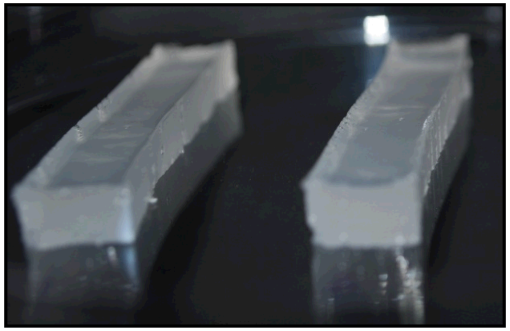
Physically Cross-linked Gel

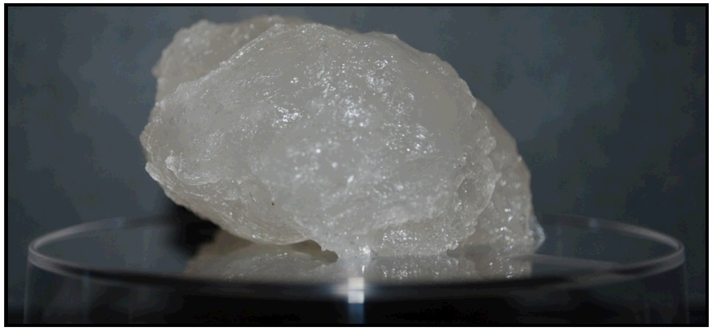
Fluorosilicone Gel

- Commercially available fluorosilicone polymer gel (adhesive)
  - Dow Corning DC4-8022 Fluorosilicone Gel

- Platinum catalyzed curing reaction
- Cured at 82 ^{o}C for 24 hours
- Gel sol fraction ≈ 50%

- Gel samples of varying hardness (equilibrium modulus) studied
  - High modulus (G_{eq} = 910 Pa)
  - Medium modulus (G_{eq} = 350 Pa)
  - Low modulus (G_{eq} = 80 Pa)

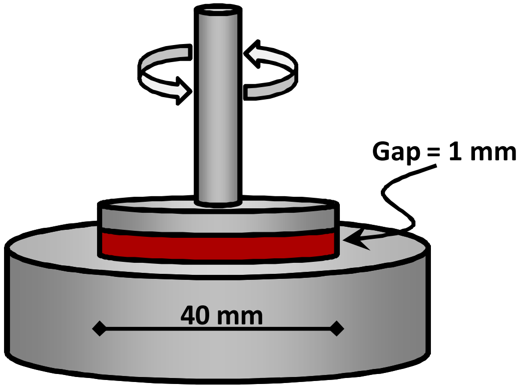




Experimental Techniques

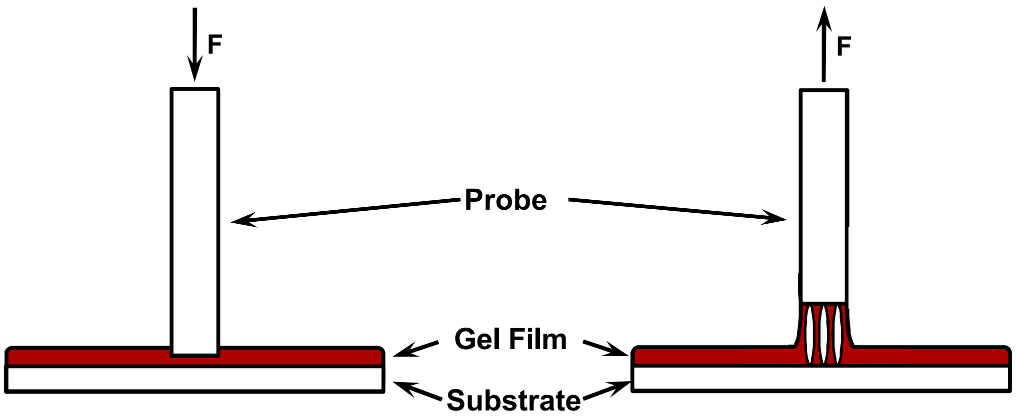
Small Amplitude Oscillatory Rheology

- TA Instruments AR-G2 rheometer
- Gel sample is cured between parallel plates with a diameter of 40 mm and a gap of 1 mm
- Oscillatory rheology measured as gel cures as well as on final cured gel
- Small amplitude oscillatory rheology allows the probing of the evolving structure of the gel without significantly disturbing it



Probe Tack Adhesion Measurement

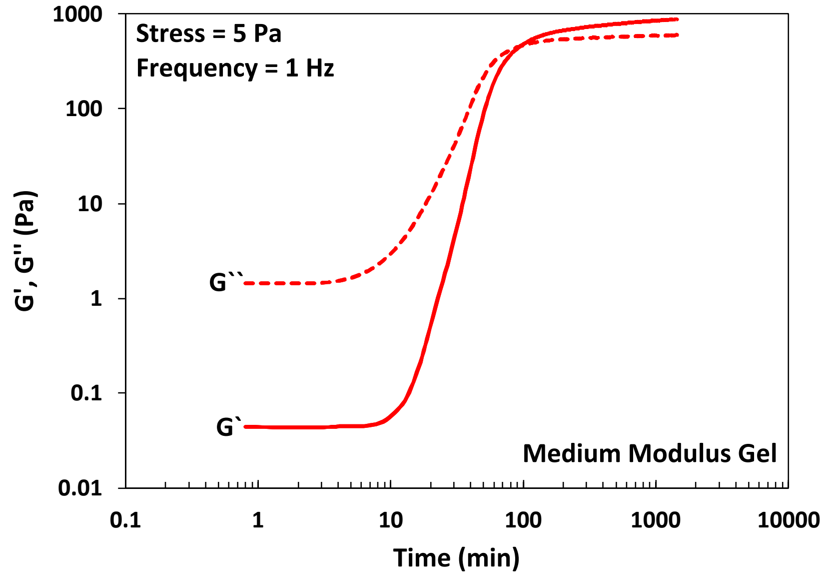
- TA Instruments ARES G2 rheometer
- 1 mm thick layer of gel cured on an aluminum plate
- 8 mm diameter probe is brought into contact with the gel film at a specified force for a specified amount of time
- Probe is then separated from the gel at a controlled rate while measuring the force as a function of distance



Curing Rheology and Gel Point Determination

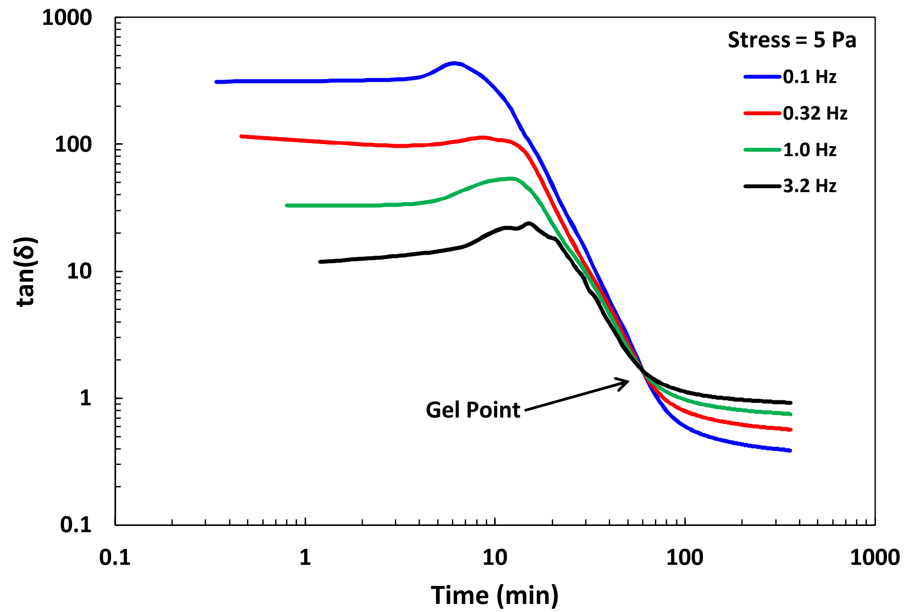
Rheology During Cure

- In the uncured gel (viscous liquid) the viscous modulus (G”) is much greater than the elastic modulus (G’)
- As the elastic gel network forms, G’ increases at a higher rate than G”
- Eventually G’ surpasses G” indicating that the material response becomes more elastic than viscous in nature

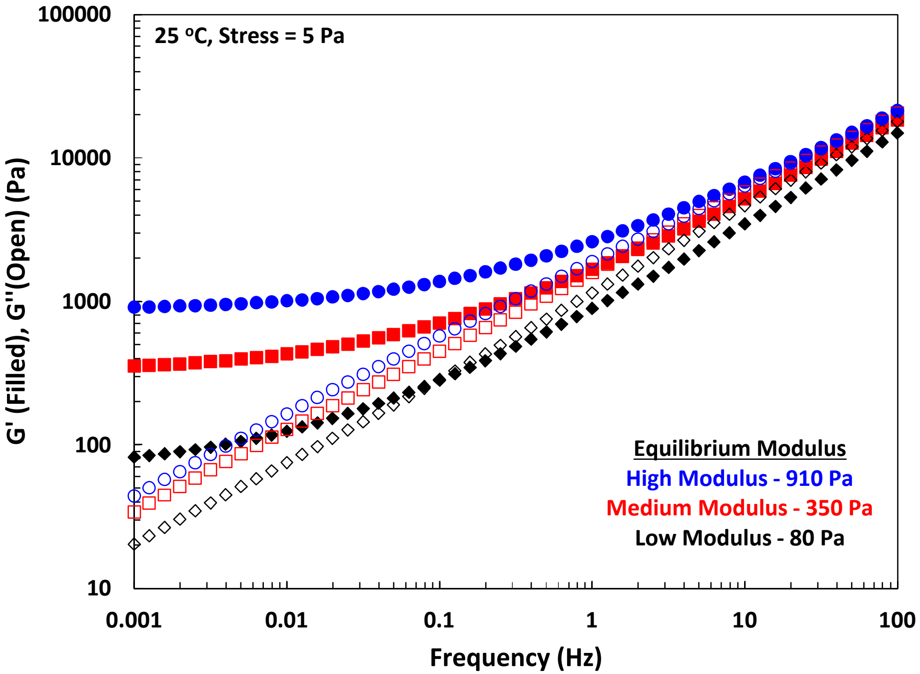


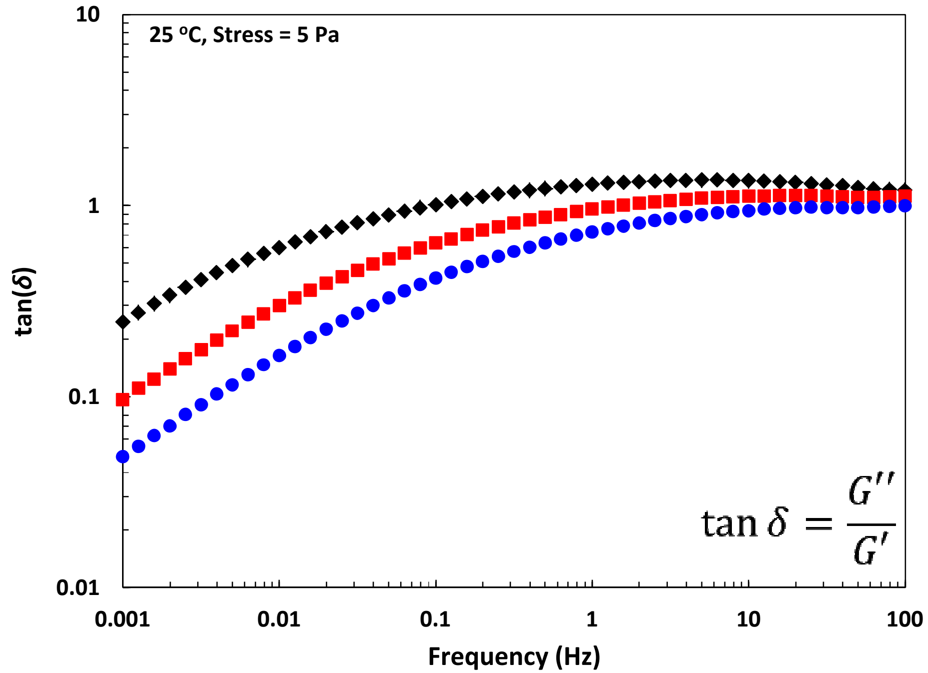
Gel Point Determination

- Gel point is the point at which a percolated polymer network is first formed
- Experimentally determined as the point at which tan(δ) is independent of frequency
- Gel time increases as the equilibrium modulus decreases



Gel Rheology





Low Frequency Response (Long Time Scales)

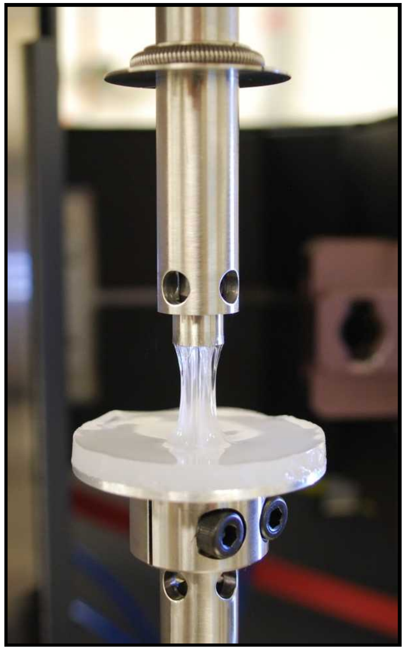
- Rheology is dominated by an elastic response from the cross-linked gel network
  - High G', low tan δ
  - High modulus gel shows greatest difference between G' and G" (smallest tan δ)
- G' is independent of frequency
  - Frequency independence used to determine the **equilibrium modulus** (G_{eq})

High Frequency Response (Short Time Scales)

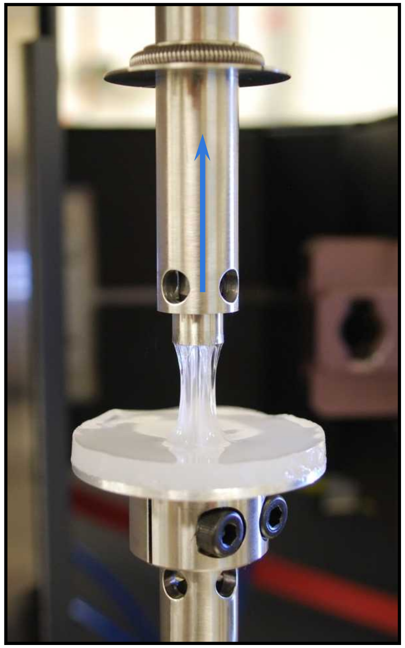
- G" exceeds G' as viscous contributions from the polymer sol become significant
- G' and G" are approximately equal (tan δ ≈ 1)
- At the highest frequencies, the material response of each gel becomes approximately equal regardless of equilibrium modulus

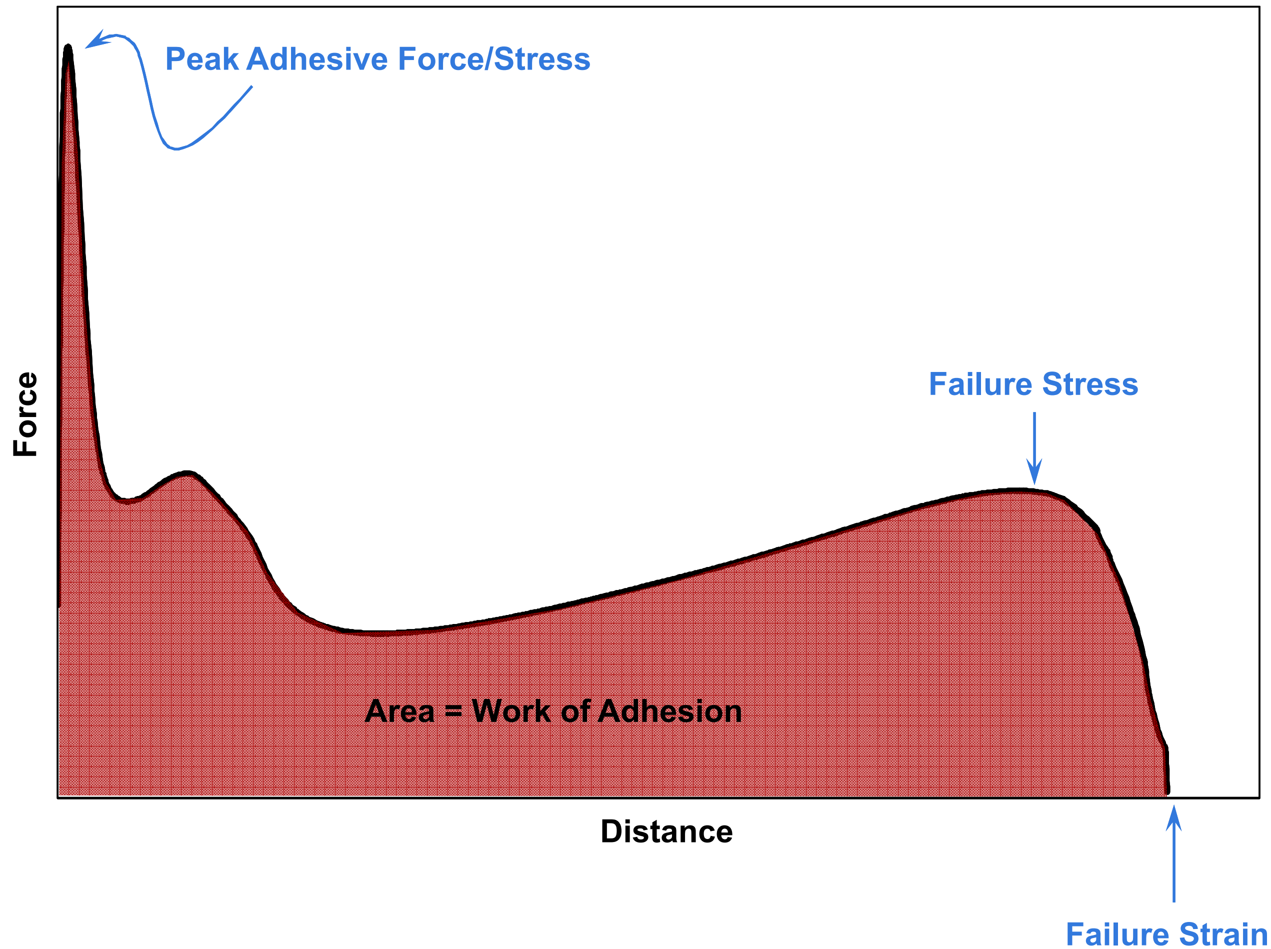
Polymer Gel Adhesion

- Lightly cross-linked polymers can form adhesive bonds of measureable strength with various surfaces
- Adhesion is highly influenced by the polymer viscoelasticity as well as surface interactions
- Adhesive effectiveness is determined by ability of the polymer to dissipate energy effectively
  - Adhesive must be able to accommodate large deformations and dissipate large amounts of energy before fracture occurs
- Here we examine the effects of **separation velocity** and **confinement** on both the adhesive properties and the debonding mechanisms observed



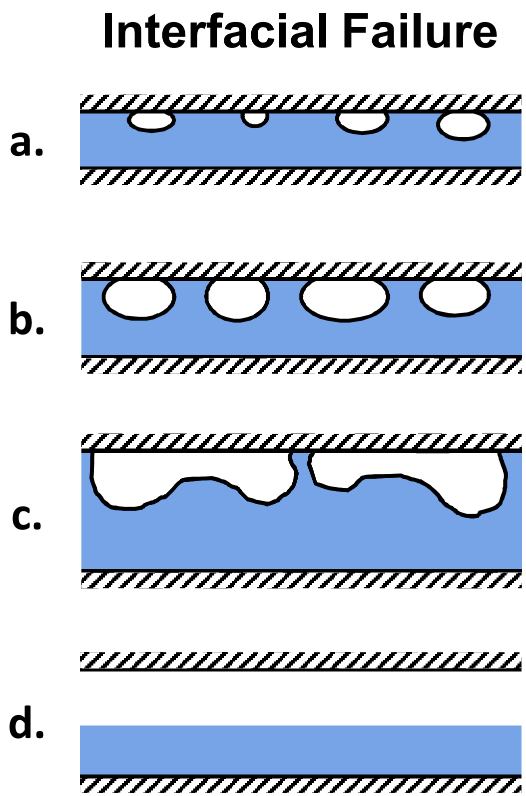
Adhesion Parameters of Interest

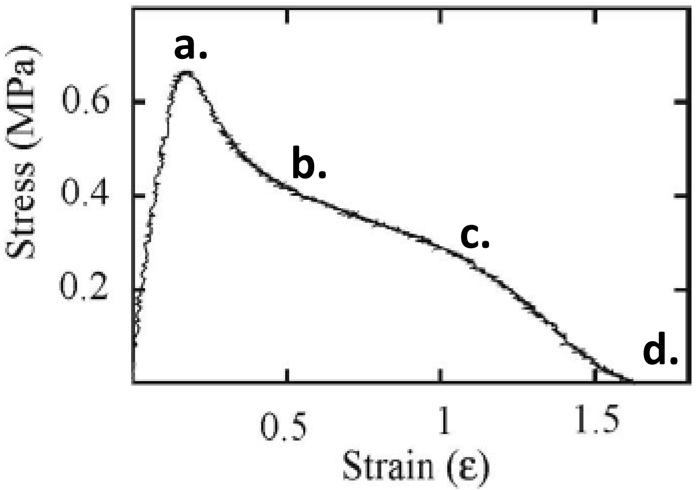




- Force – distance (and associated stress – strain) curve provides several key properties
- Overall shape of the stress – strain curve is also indicative of debonding mechanism

Debonding Mechanisms – Interfacial





a. Cavities form via surface cavitation or expanding of existing defects on probe surface

b. Cavities grow larger as the sample is strained

c. Cavities coalesce, decreasing surface contact with probe

d. Upon complete debonding the adhesive film is undamaged

Brown et al., *Macromol. Mater. Eng.* **2002**, 287, 163-179

Debonding Mechanisms – Bulk

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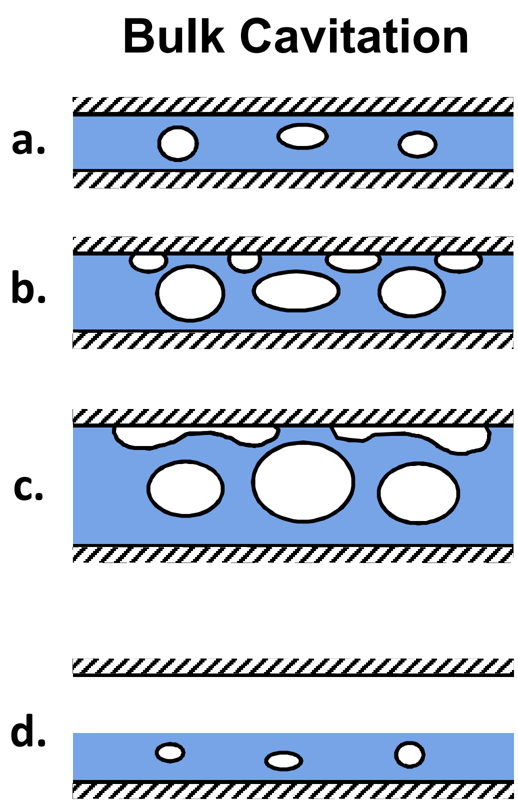

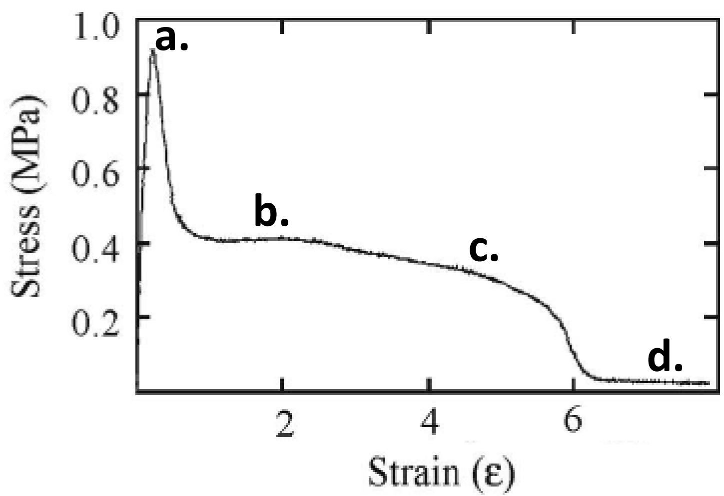

a. Stress build up in the adhesive layer exceeds the threshold for cavitation and cavities form within the bulk which relieves stress

b. Bulk cavities grow and interfacial cavities form (initial stages of interfacial failure)

c. Interfacial cavities coalesce, decreasing surface contact with probe

d. Upon complete debonding the adhesive film is undamaged, but bubbles remain in the bulk material at the bulk cavitation sites

Brown et al., *Macromol. Mater. Eng.* **2002**, 287, 163-179

Debonding Mechanism Changes with Confinement

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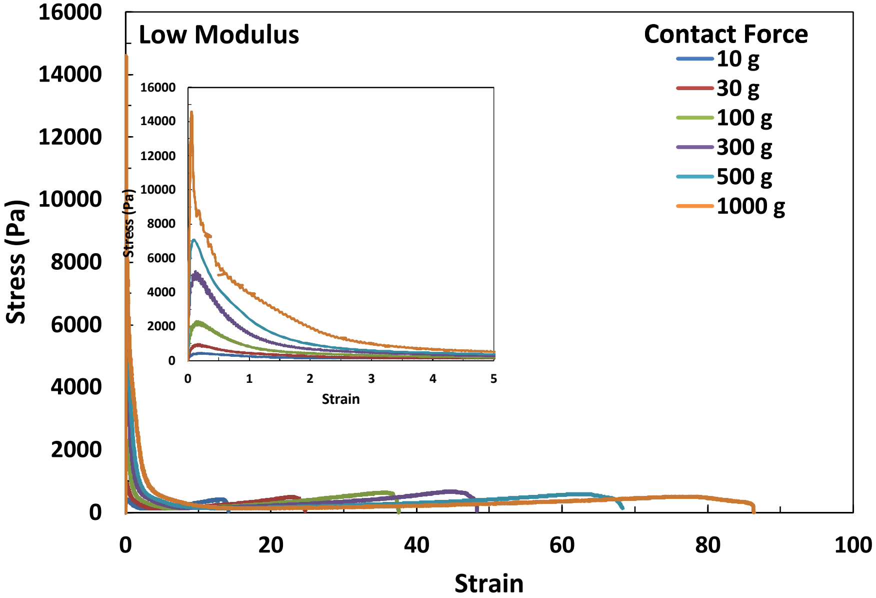
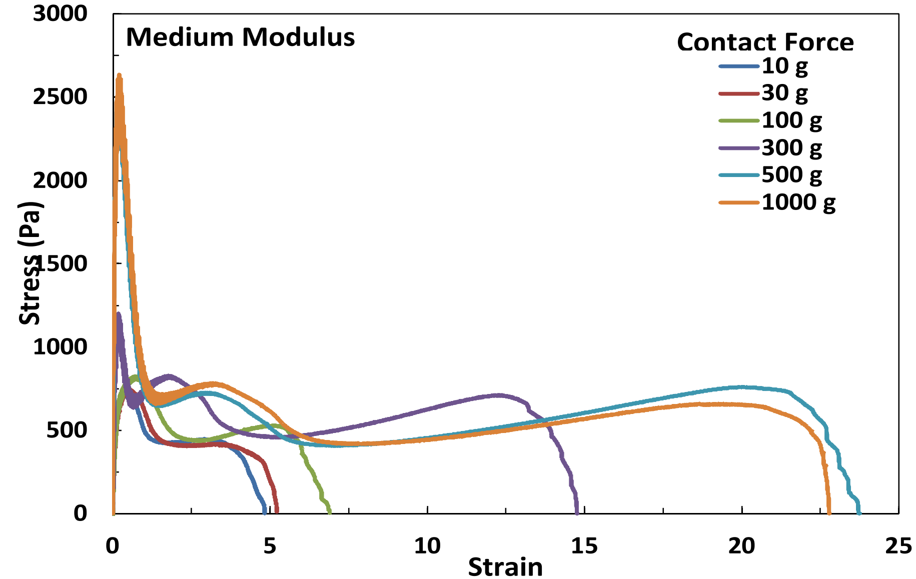
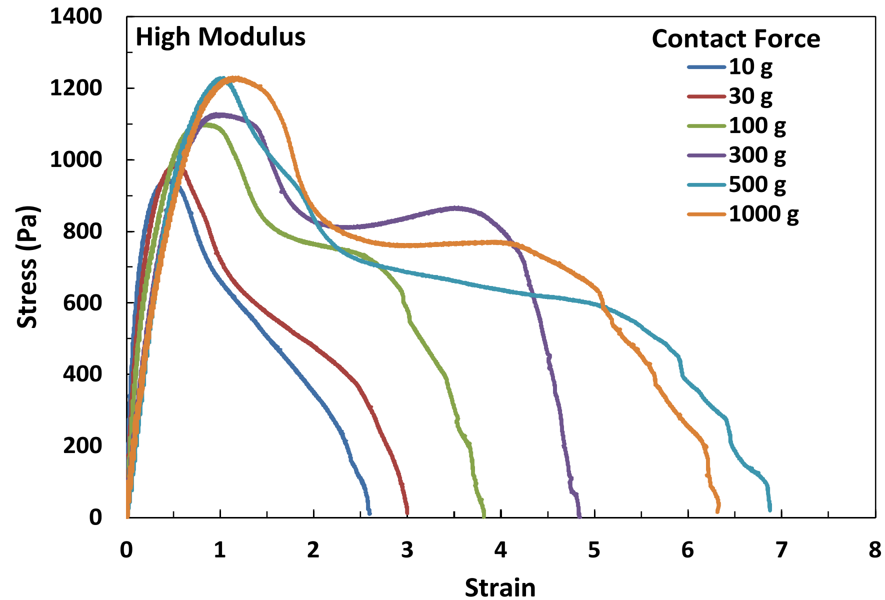


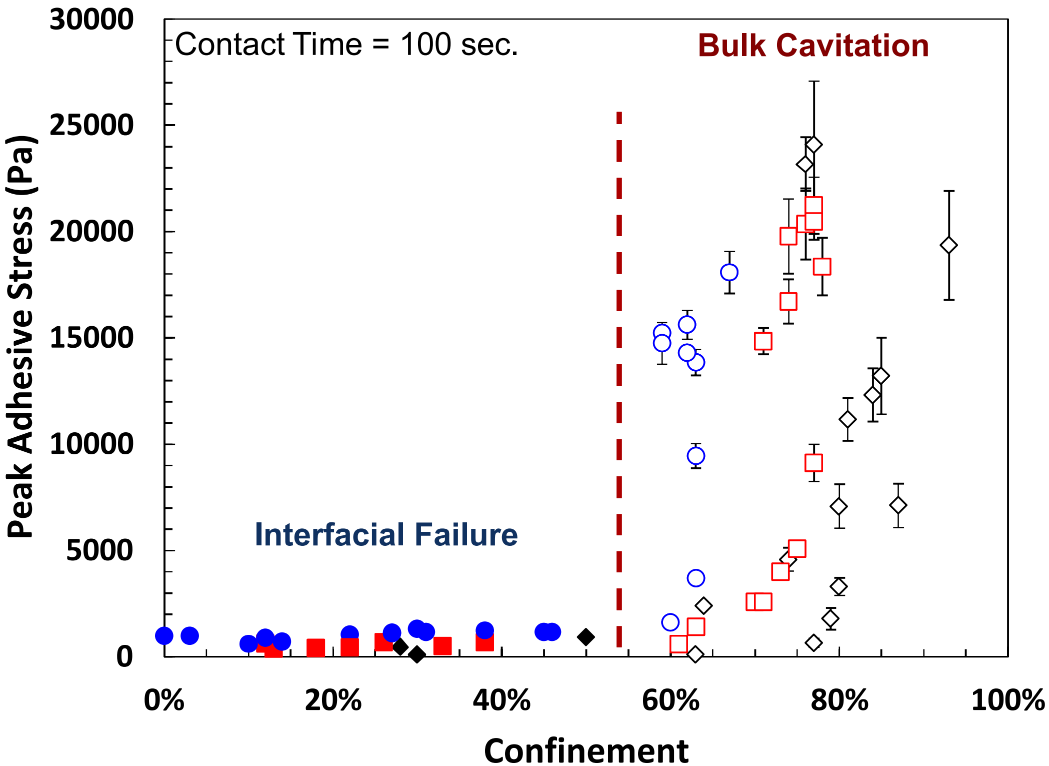


Debonding is determined by both confinement and material properties

- Low modulus gel (above) exhibits bulk cavitation at all but the smallest contact force (confinement)
- Medium modulus gel (above right) exhibits the transition region between interfacial debonding and bulk cavitation
- High modulus gel (right) exhibits interfacial failure at all values of confinement tested



Confinement Effects



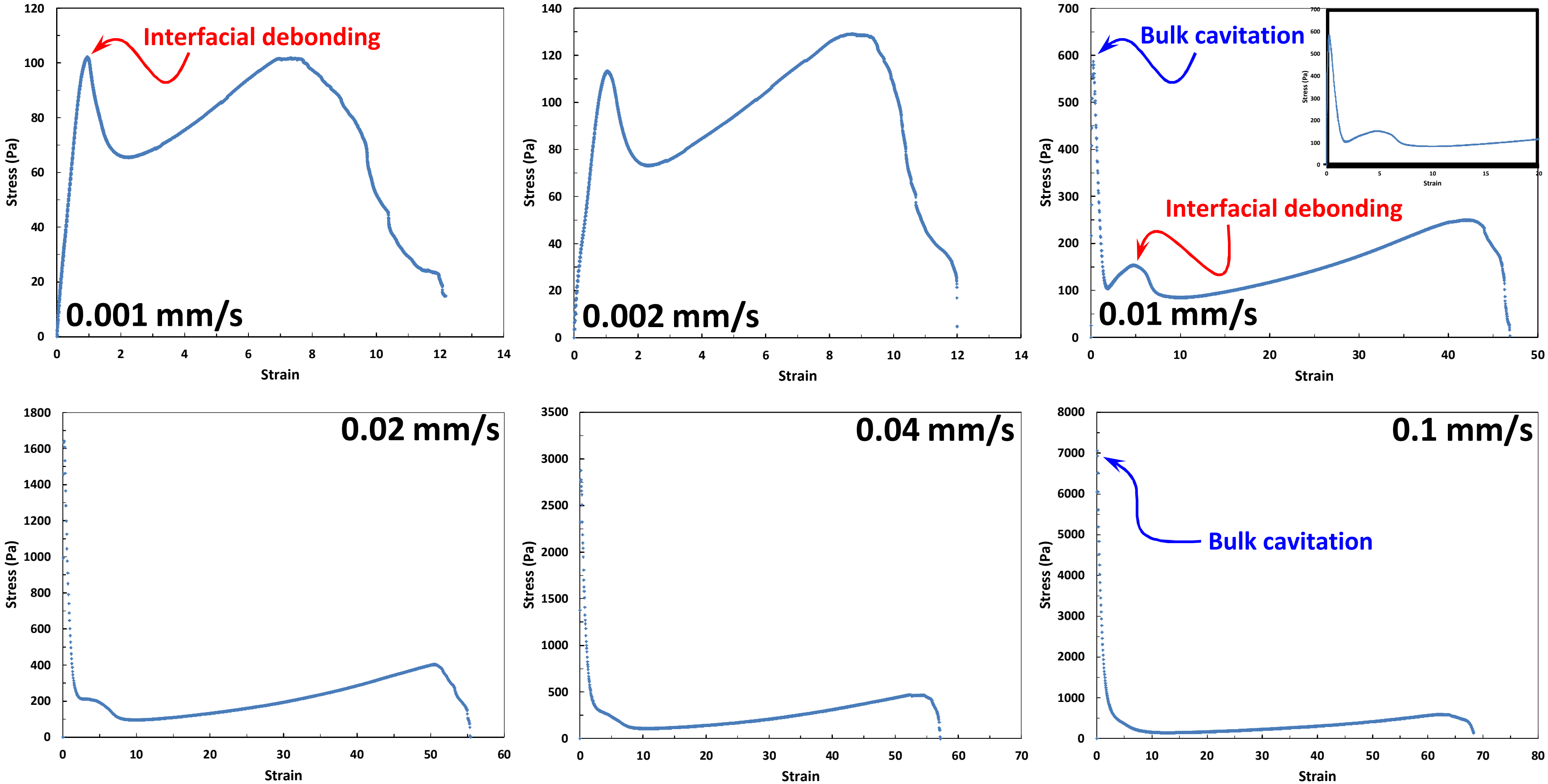
$$Confinement = \left(1 - \left(\frac{h}{h_o}\right)\right) \times 100$$

h = height at point where measured force changes sign
h_o = original film thickness

- For confinement below 50%, the peak adhesive force is independent of confinement
- Interfacial failure is the dominant debonding mechanism
- Above about 60% confinement, the peak adhesive force increases sharply with confinement
- Bulk cavitation is the dominant debonding mechanism
- All gels exhibit a similar confinement threshold where the debonding mechanism changes from interfacial to bulk cavitation, regardless of equilibrium modulus

Debonding and Separation Velocity

Low modulus gel, Contact force = 500 g, Contact time = 100 sec.

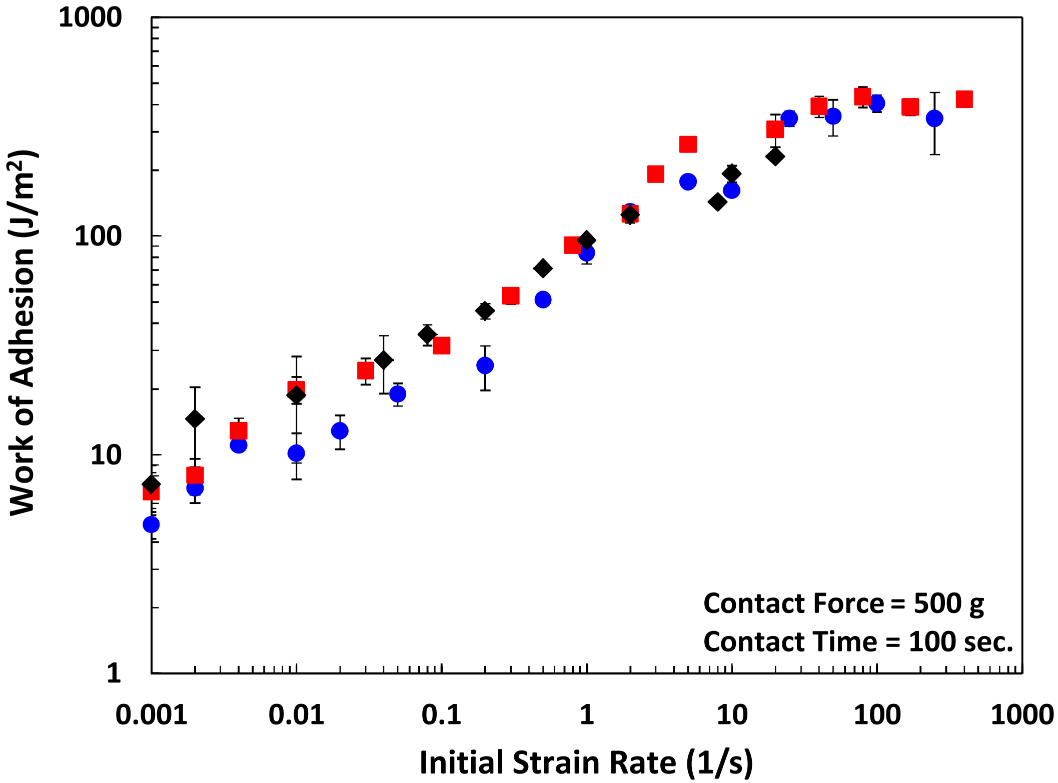


- As the separation velocity increases, the dominant debonding mechanism shifts from interfacial debonding to bulk cavitation
- At intermediate separation velocities, a transition region is observed where both mechanisms are manifest

Time Scale Effects

- Work of adhesion depends strongly on the speed that the probe is separated from the polymer film
- At low and moderate initial strain rates, a power law dependence is observed

- At high initial strain rates, the work of adhesion is independent of initial strain rate
- Work of adhesion for all three gels converges to a similar value
  - Consistent with rheological observations at short time scales (high frequencies)
  - Short time scales do not allow the polymer sol to relax so the contribution from physical entanglements in the sol become significant



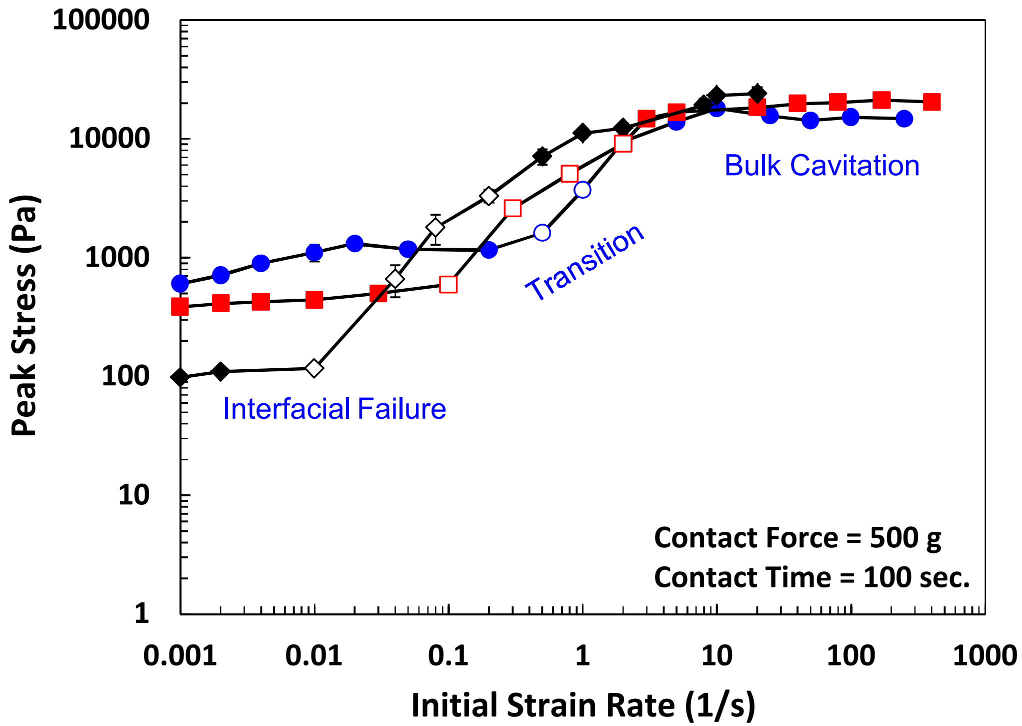
Peak Stress Also Depends on Time Scale

Low Initial Strain Rates

- Peak stress is independent of initial strain rate
  - **High modulus** gel exhibits highest peak stress
  - Time scale of the deformation is slow enough that viscous contributions from polymer sol can be neglected
  - High modulus gel exhibits highest peak stress due to higher elastic modulus (more elastic gel network)

High Initial Strain Rates

- Peak stress is independent of initial strain rate
  - **Low**, **Medium**, and **High** modulus gels all exhibit the same peak stress values
  - This convergence is consistent with the work of adhesion and the rheology at short time scales
  - All three gels behave similarly at very short time scales



Intermediate Initial Strain Rates

- Power law dependence of peak stress on initial strain rate
  - Power law region is characterized by a transition in debonding mechanism from interfacial failure to bulk cavitation

Another Look at Peak Stress

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Low Initial Strain Rates

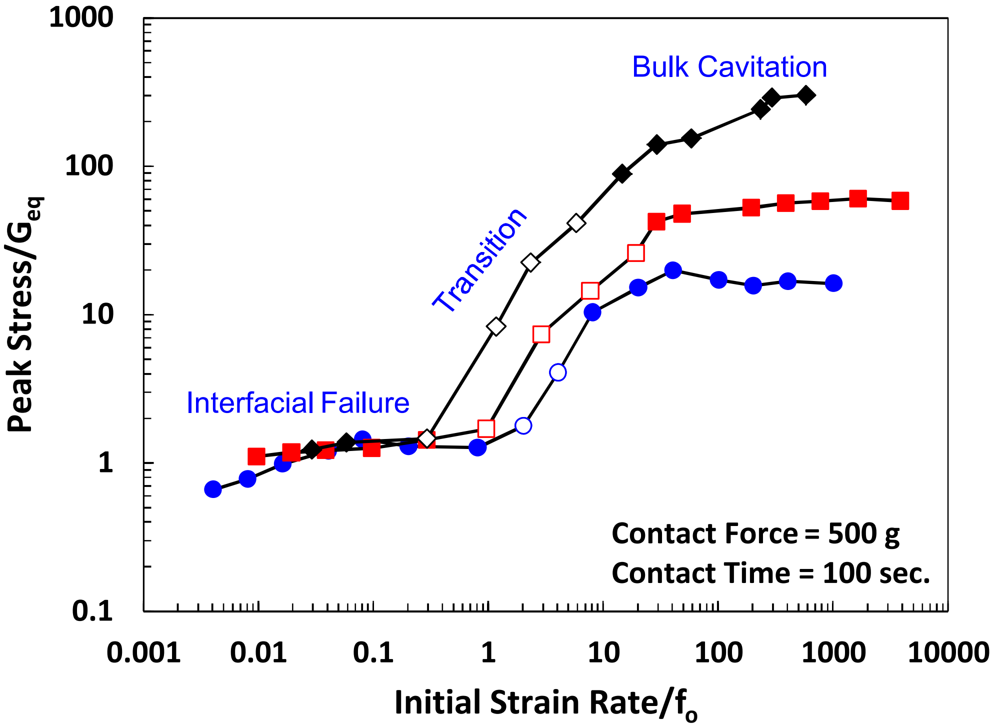
- Peak stress is independent of initial strain rate
- Peak stress/G_{eq} is constant for all gels
  - In the regime where interfacial failure dominates, the peak stress generated is proportional to the equilibrium modulus
  - Peak adhesive stress in this regime is a material property rather than a product of the experiment

Intermediate Initial Strain Rates

- Power law dependence of peak stress on initial strain rate
  - Transition between debonding mechanisms

High Initial Strain Rates

- Peak stress is independent of initial strain rate
- Peak stress values differ from one another – peak stress in bulk cavitation regime is NOT a material property



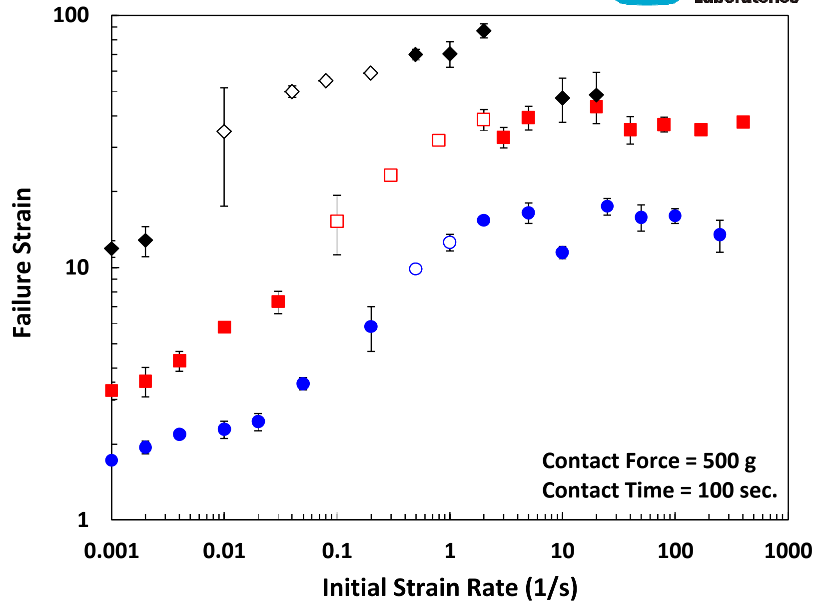
Peak stress normalized by the equilibrium modulus (G_{eq})

Initial Strain rate normalized by a characteristic frequency (f_o) determined from tan δ curves for each gel

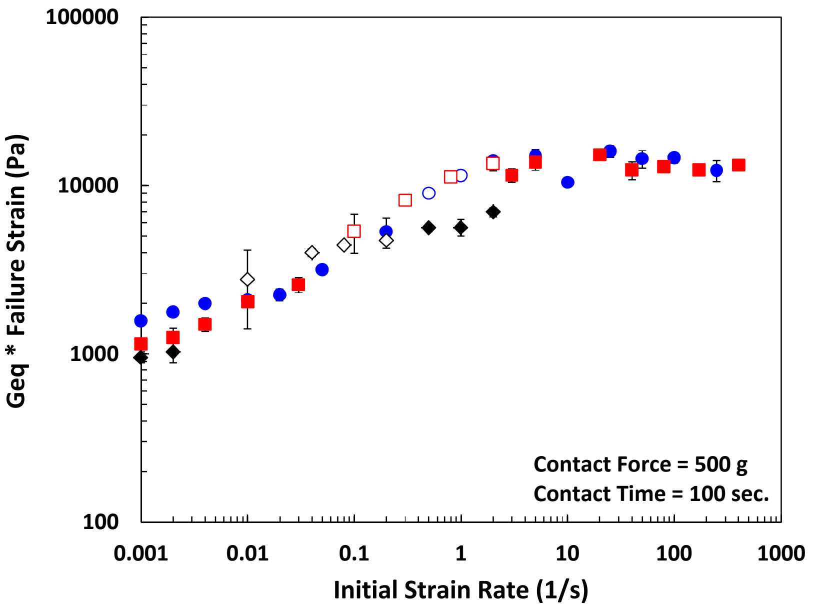
f_o = frequency at which viscous effects become significant

Strain to Failure

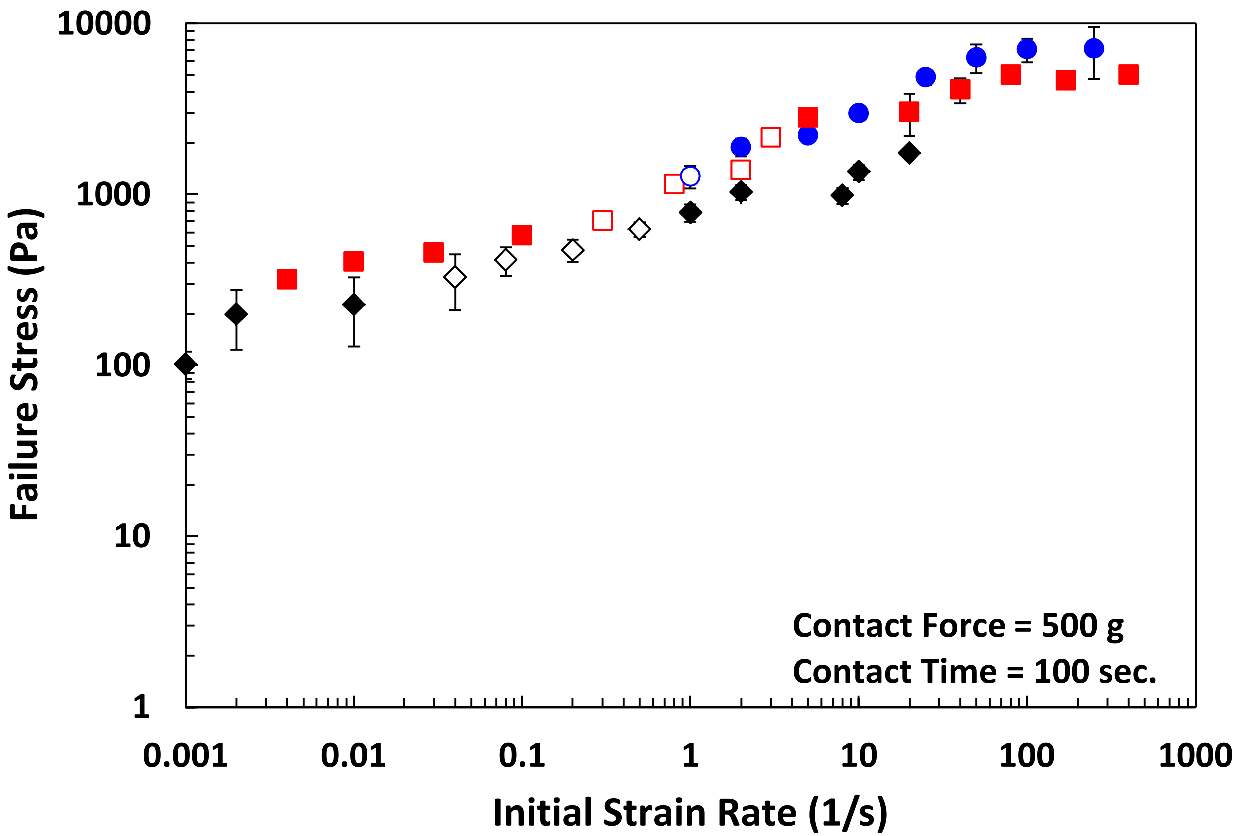
- Failure strain is independent of initial strain rate for high strain rates
  - Bulk cavitation also the dominant debonding mechanism
  - Similar to behavior observed in rheology and work of adhesion
- Power law dependence on initial strain rates at low and intermediate rates



- When the failure strain is multiplied by the equilibrium modulus, the three curves collapse to a single curve
- Failure strain is an intrinsic material property for these gels across all initial strain rates
- Independence of strain rate observed at high rates
- These data suggest that, for a given initial strain rate, each gel fails at a common stress stored in the elastic network



Stress at Failure



- Stress at failure shows the same qualitative dependence on initial strain rate as the product of the equilibrium modulus and failure strain
- Power law dependence at low and intermediate rates followed by independence of rate at high strain rates
- These dependencies are qualitatively similar to those observed in the rheology (tan δ) and work of adhesion

Summary

- Adhesive properties and debonding mechanisms of fluorosilicone polymer gels are sensitive to both the **confinement** of the gel and the **separation velocity**

Low Confinement or Low Initial Strain Rate

Debonding mechanism is dominated by **interfacial failure**

Work of adhesion, failure strain, and failure stress show **power law dependence** on initial strain rate

High Confinement or High Initial Strain Rate

Debonding mechanism is dominated by **bulk cavitation**

Work of adhesion, peak adhesive force, failure strain, and failure stress show **independence** of initial strain rate

Intermediate Initial Strain Rate

Transition regime where debonding is influence by **BOTH interfacial failure and bulk cavitation**

Transition in debonding mechanism is evident in the dependence of work of adhesion, peak adhesive stress, and failure strain

Also evident in the shape of the stress – strain curve