Technique for Monitoring Environmentally Induced Changes in Polymeric Sealants

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Introduction

Project Objective

Experiments

Results

- **Phase 1: Molecular level changes**
- **Phase 2: Macroscopic changes**

Conclusion

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Introduction

◆ What is a sealant ?
- Elastomer used to prevent moisture intrusion into a structure

- Widely used throughout most structures
- 30 billion dollar a year industry
- 420,000 tons produced per year

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Challenge

- Current materials are good, but eventually fail

→

- **55%** fails within **10 years**
- **95%** fails within **20 years**

Don’t know its failed until you see extensive water damage

- Modern architecture increases Challenge
  - Much more difficult to seal
  - Much more sealant required
  - Often requires structural performance

Guggenheim Museum in Bilbao, Spain

Old vs. new

- **Critical Need – <u>Measure durability & predictive models.</u>**

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Metrology

- Outdoor Aging

- Problem
  - Time consuming
  - Never get same conditions twice
- Laboratory Accelerated Aging

Make Comparison
Outdoor
Vs.
Accelerated Aging

- Historically correlation very poor
- Need well controlled laboratory tests

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Metrology

- Outdoor Aging

Make Comparison
Outdoor
Vs.
Accelerated Aging

SPHERE: Simulated Photodegradation by High Energy Radiant Exposure

- Problem
  - Time consuming
  - Never get same conditions twice
- Laboratory Accelerated Aging
  - NIST SPHERE - Complete control of
    - » Light (UV radiation) – up to 10 or 20 times sunshine
    - » Temperature
    - » Humidity

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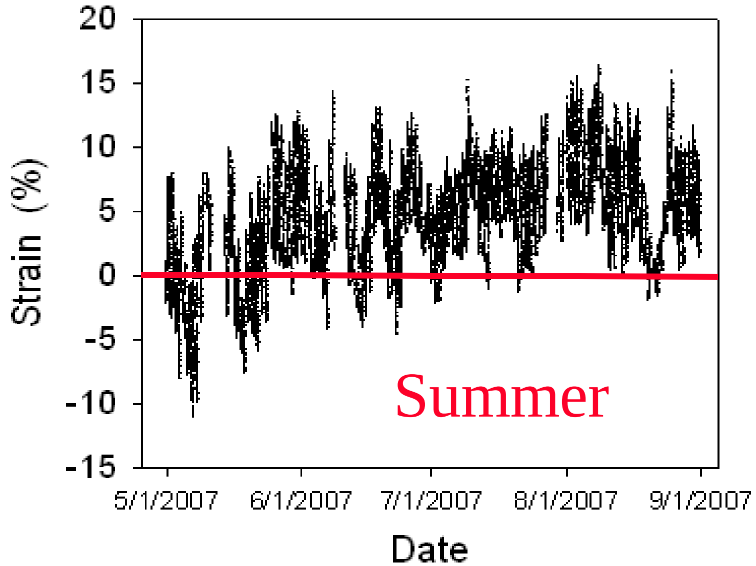
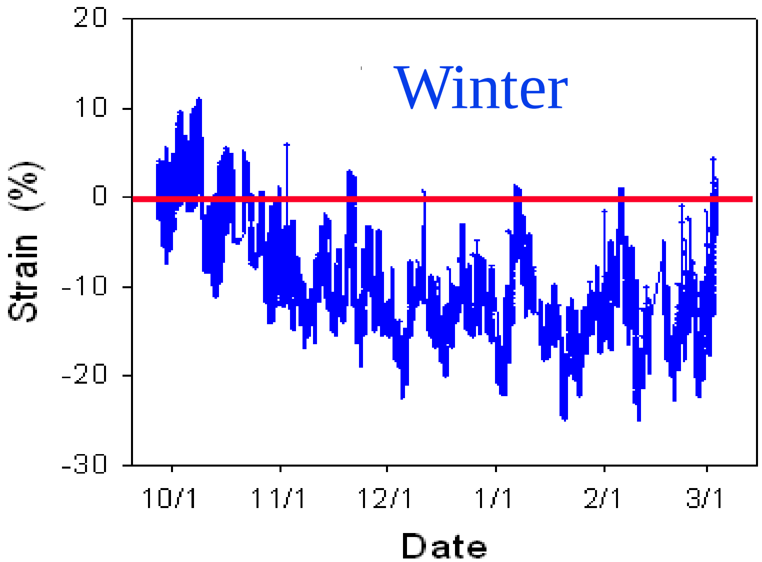
Exposure to Motion

- Successful with coatings but sealants have added variable – continuously changing strain
  - Wood structures, strain driven by humidity
  - Other materials driven by temperature

- Temperature Effect in sealant designed for ± 25 % strain





  - Daily cycle range 7 % strain
  - Yearly cycle range 25 % strain

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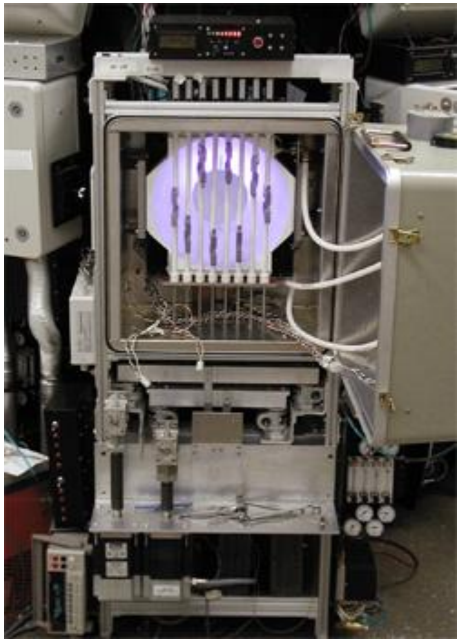
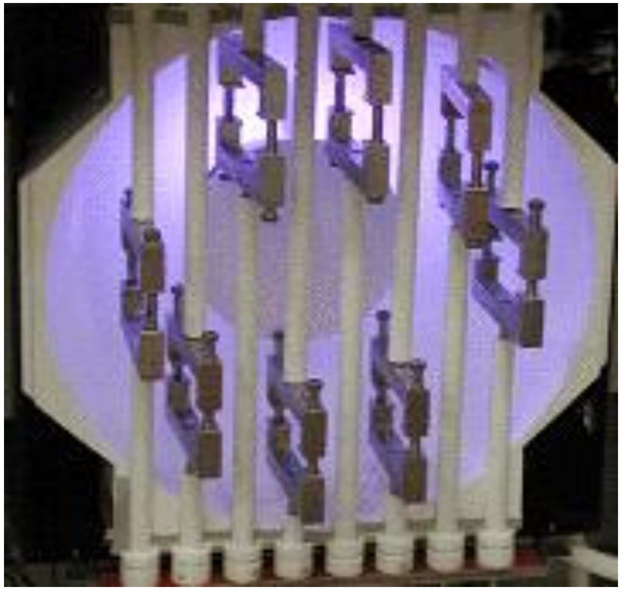
Motion Control During Exposure

- Adapt device to allow programmed motion of sealants in chamber before, during, and after exposure





- Challenge: Monitor properties as a function of exposure time – look for changes
- Many properties of interest but talk will focus on mechanical behavior

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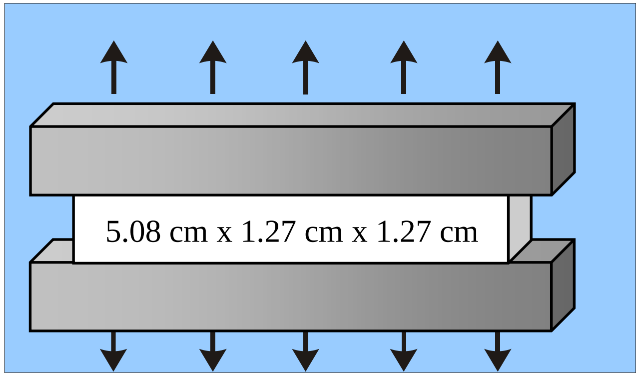
Program Objective

- Develop mechanical characterization technique to monitor changes
  - Phase I: Molecular level changes - possibly
    - » Effective cross-link density
    - » Glass to rubber transition
    - » Rubber to fluid transition
    - » Heterogeneity
  - Phase II: Macroscopic changes
    - » Cracks and debonding

- Test geometry



  - Advantage: Widely used and accepted by industry (ASTM C719)
  - Disadvantages: not a uniform strain field
  - Apparent Modulus, E_a, is related to tensile modulus, E, by shape factor, S

$$E_a = S\ E$$

  - Need only E_a to follow changes

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Experiments

- Phase 1: Develop technique to monitor modulus - provides insight into molecular level changes
  - 3 challenges to overcome
  - Materials: 5 different sealants
    - » Composition unknown, but
    - » Span the range of chemistries and formulations in commercial materials designated Sealants 0, 2P, 3P, 4P, & 5P
- Phase 2: Extend technique to macroscopic changes
  - Two Tasks: Model development and exposure studies
  - Materials – composition unknown
    - » Exposure Studies: material selected from many industry supplied candidates
      - Typical of commercial materials except but formulated to be susceptible to environmentally induced changes – designated Sealant 2
    - » Model Development: material available in sufficient quantities - designated Sealant 1

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Phase 1: Test Development

- 3 Challenges
  - Reversibility
  - Mullins Effect
  - Test Method Selection

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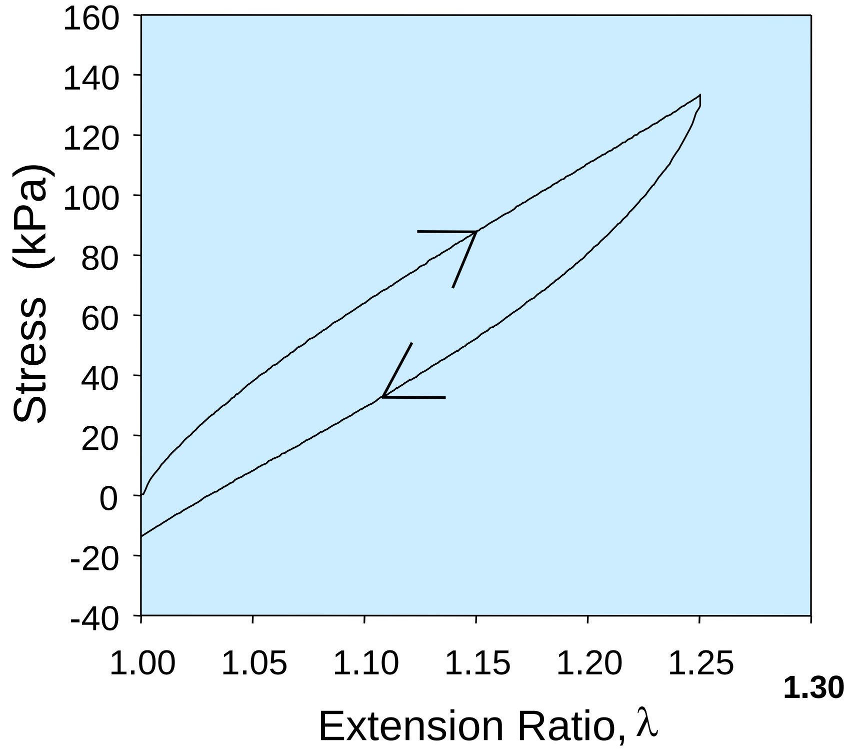
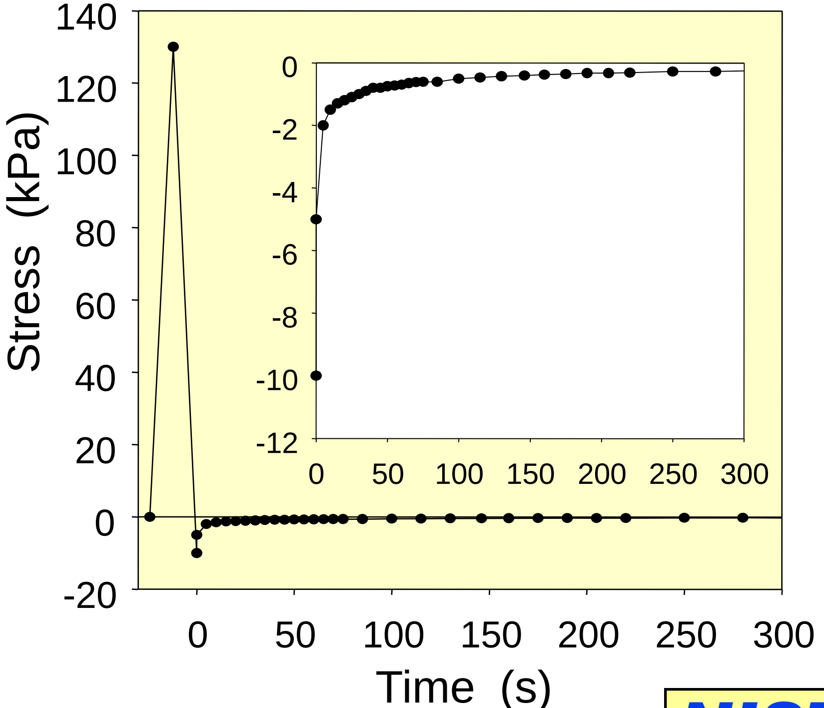
Challenge 1: Recovery



- Stress – Strain Curves
- When strain returns back to 0, some compressive stresses are generated.
- Monitor recovery (stress decay)



- Deformations recoverable:
  - Stresses rapidly reduce to zero (<1 % of maximum load) – **Full recovery.**
  - **Time scale for recovery is typical of that for viscoelasticity: Loaded t_o – recovery $10\ t_o$ (to = 30 s)**

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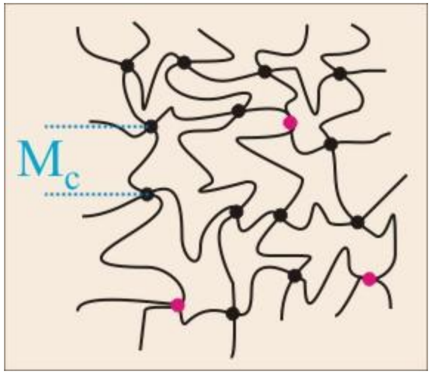
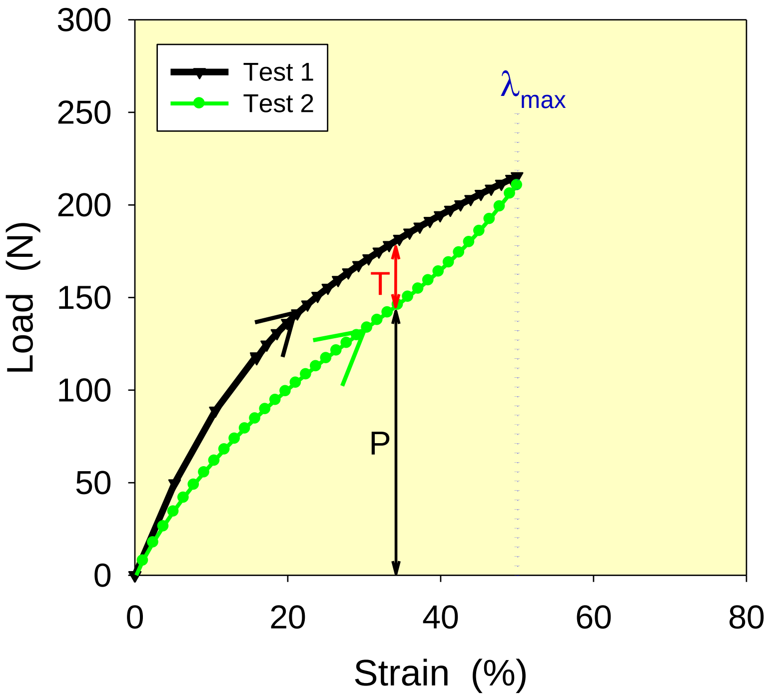
Challenge 2: Mullins Effect

- Load to a maximum stress, λ_{max}
- Second loading curve is different than first – Mullins Effect
- Magnitude is T/(T+P)

Junction Points
Permanent
Temporary





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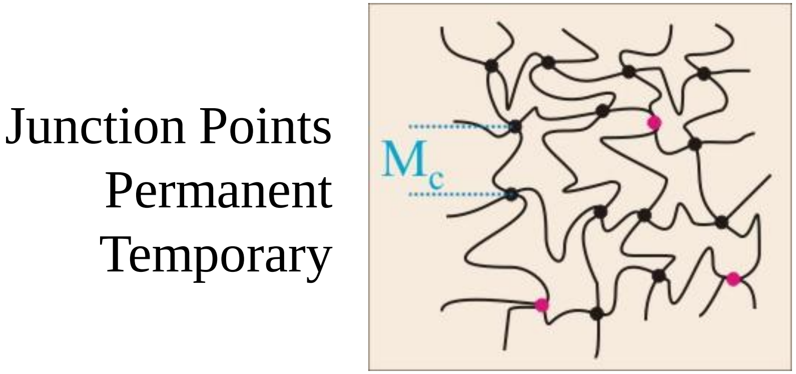
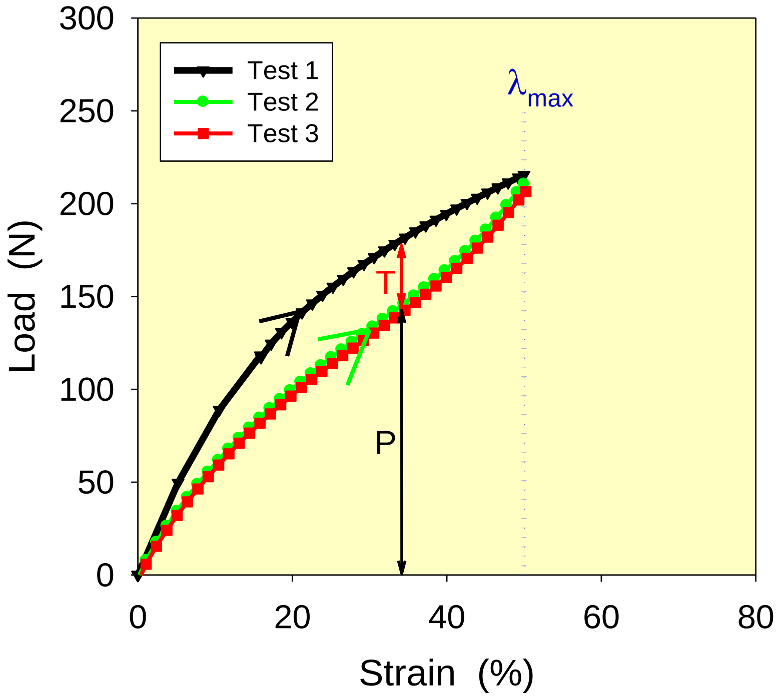
Challenge 2: Mullins Effect

- Load to a maximum stress, λ_{max}
- Second loading curve is different than first – Mullins Effect
- Magnitude is T/(T+P)
- Subsequent loading curves same as second if $\lambda > \lambda_{max}$
- **Consequently, the usual test procedure is to preload to high strain then test at $\lambda > \lambda_{max}$**





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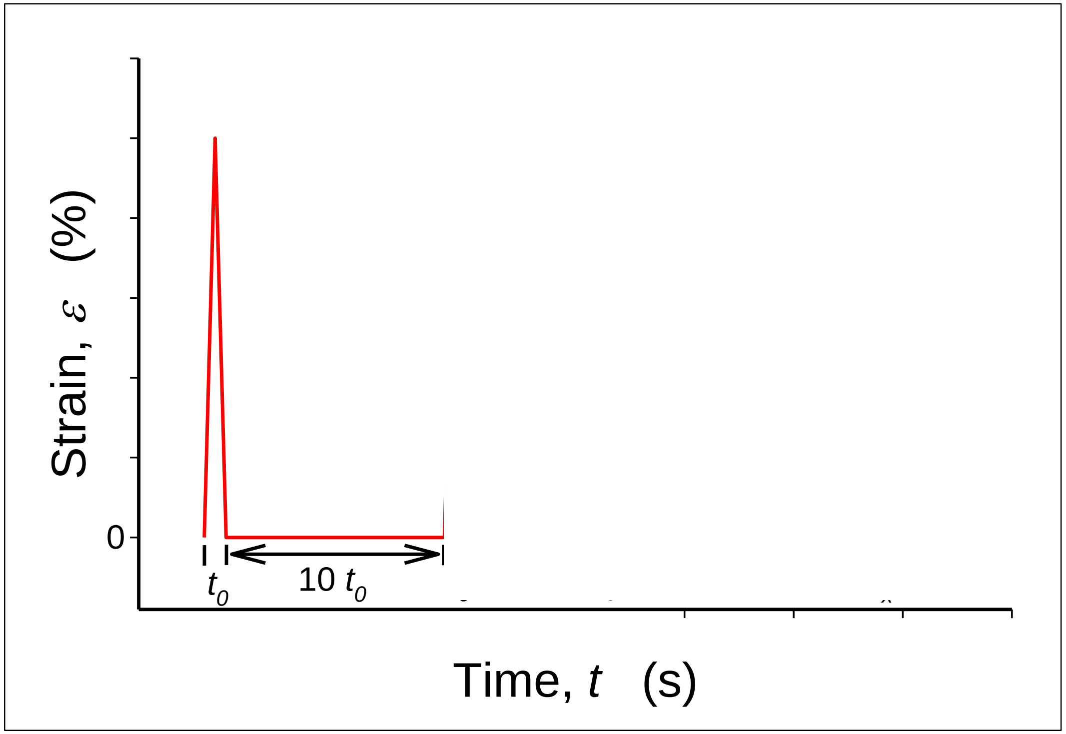
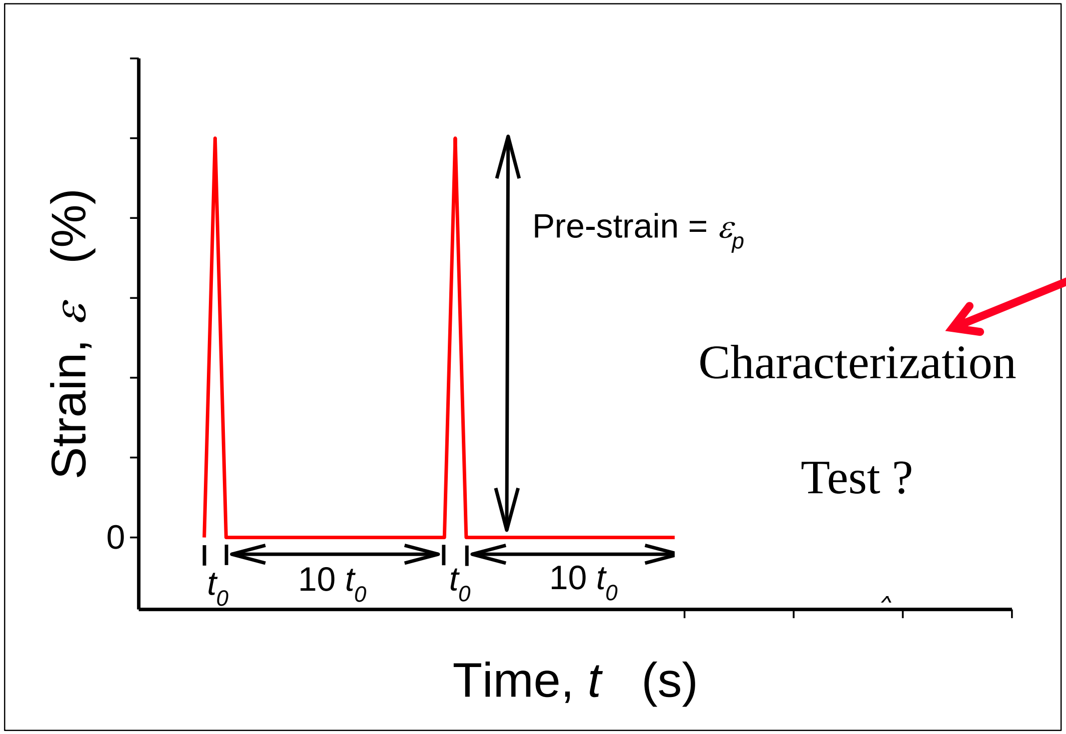
Initial Preconditioning

- One load-unload-recover cycle eliminates Mullins Effect



Initial Preconditioning

- One load-unload-recover cycle eliminates Mullins Effect
- Two cycles both eliminate and characterize Mullins Effect
- Can see why complete recovery is important



Next Challenge

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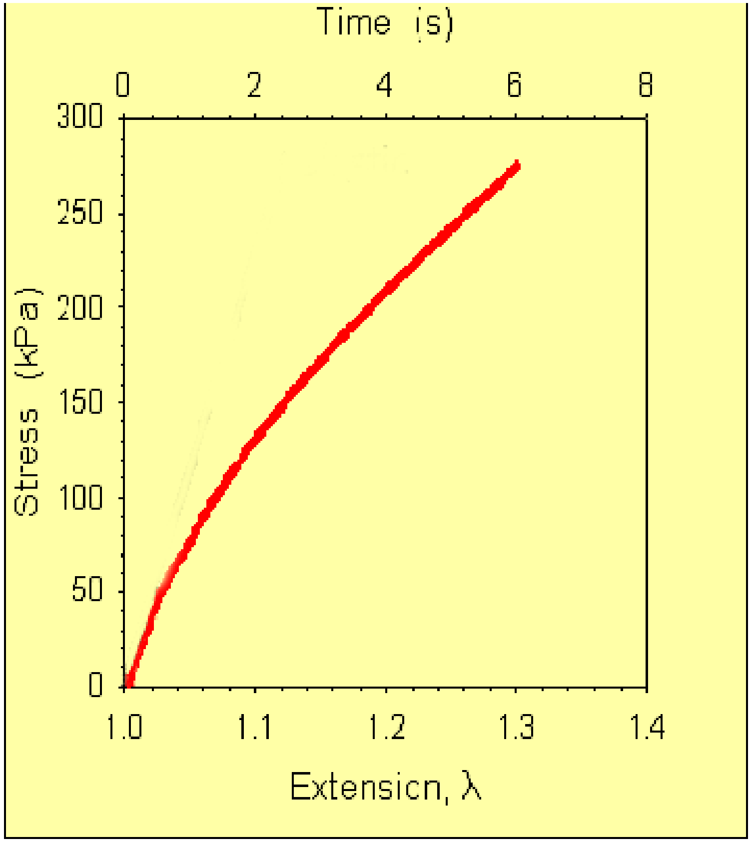
Challenge 3: Test Method Selection

- Stress-strain curves are non straight lines so not linear elastic.
  - Time effect (viscoelastic)
  - Strain level effect (non-linear)
  - Both
- Test method needs to separate the effects of time and strain level



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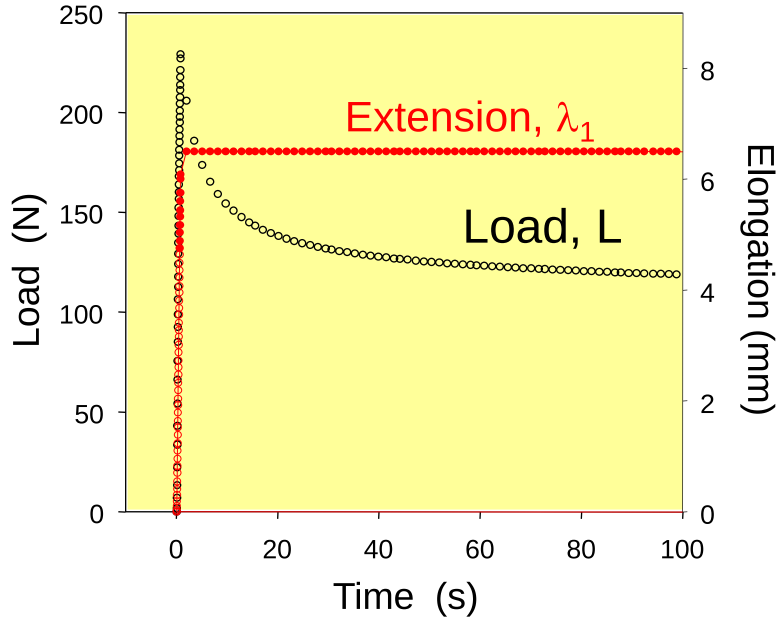
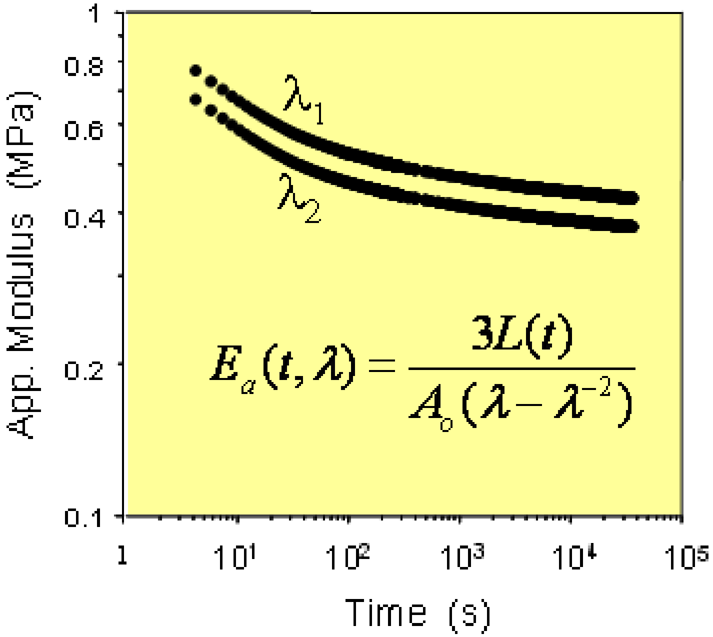
Stress Relaxation Test - Characterization

- Apply step strain, ε, or extension ratio, λ $(=1+\varepsilon)$, and monitor load, L, as a function of time, t.
- Calculate Apparent Modulus, $E_a(t,\lambda) = \dfrac{3L(t)}{A_0(\lambda - \lambda^{-2})}$ and plot vs time.
- Repeat at different strains, λ_2, etc.





- **Curve gives time dependence at a fixed strain - viscoelasticity**
- **Vertical lines show strain dependence at a fixed time – non-linearity.**

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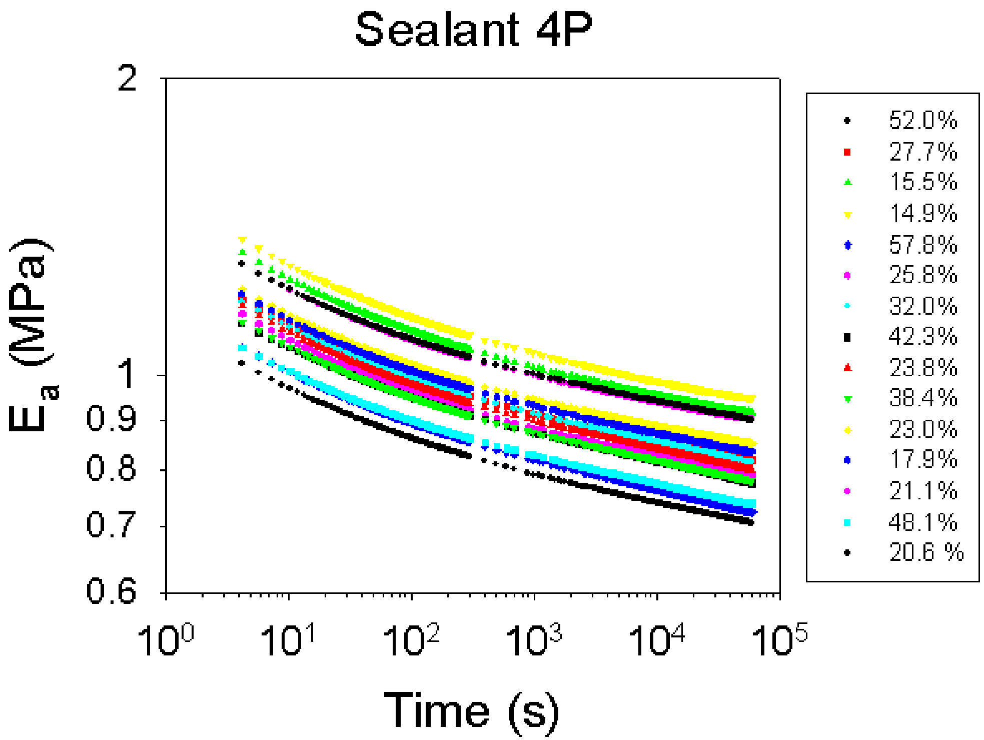
Sample Results

- Strain levels curves are parallel <u>in range tested</u>
- Time dependence (curve shape) independent of strain level - separability



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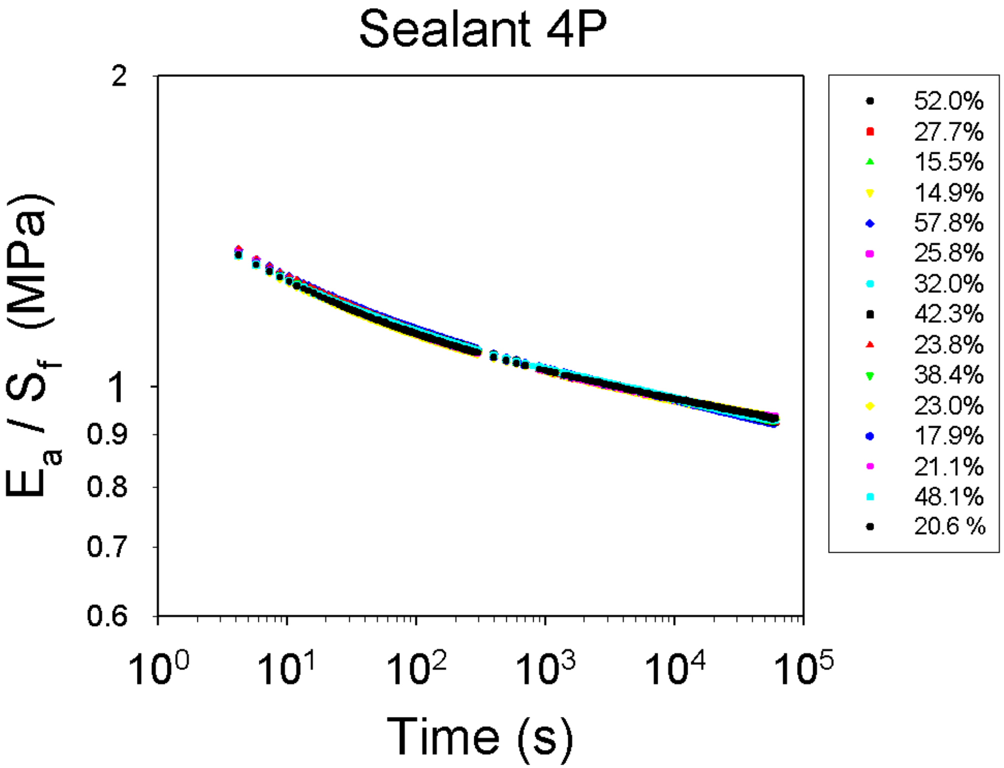
Sample Results

- Strain levels curves are parallel <u>in range tested</u>
- Time dependence (curve shape) independent of strain level - separability
- Can shift vertically to get master curve
- **Is the behavior general or limited to this material ?**



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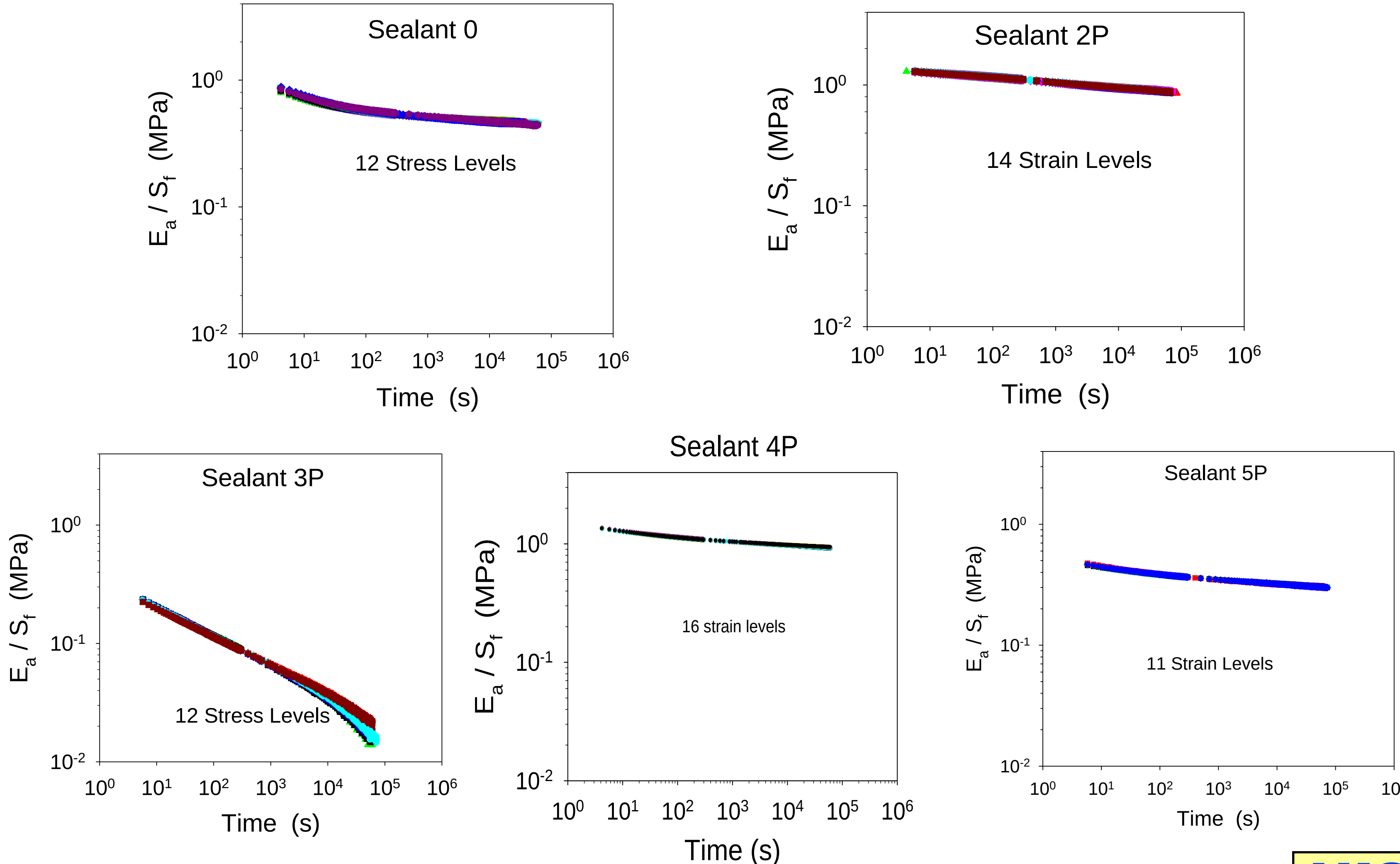
Master Curves possible for all 5 sealants



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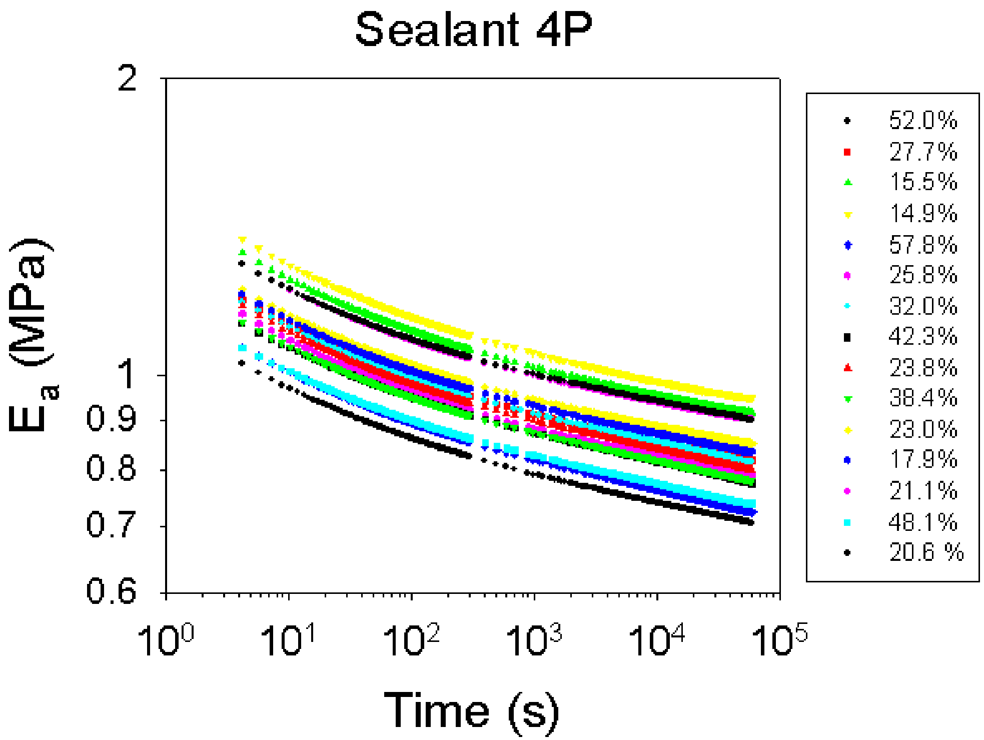
Test Strain Selection

- Time dependence provides most direct information on molecular level parameters
- Since time dependence (curve shape) is same for all strain levels in tested range
- We need test only one strain level to get information we desire



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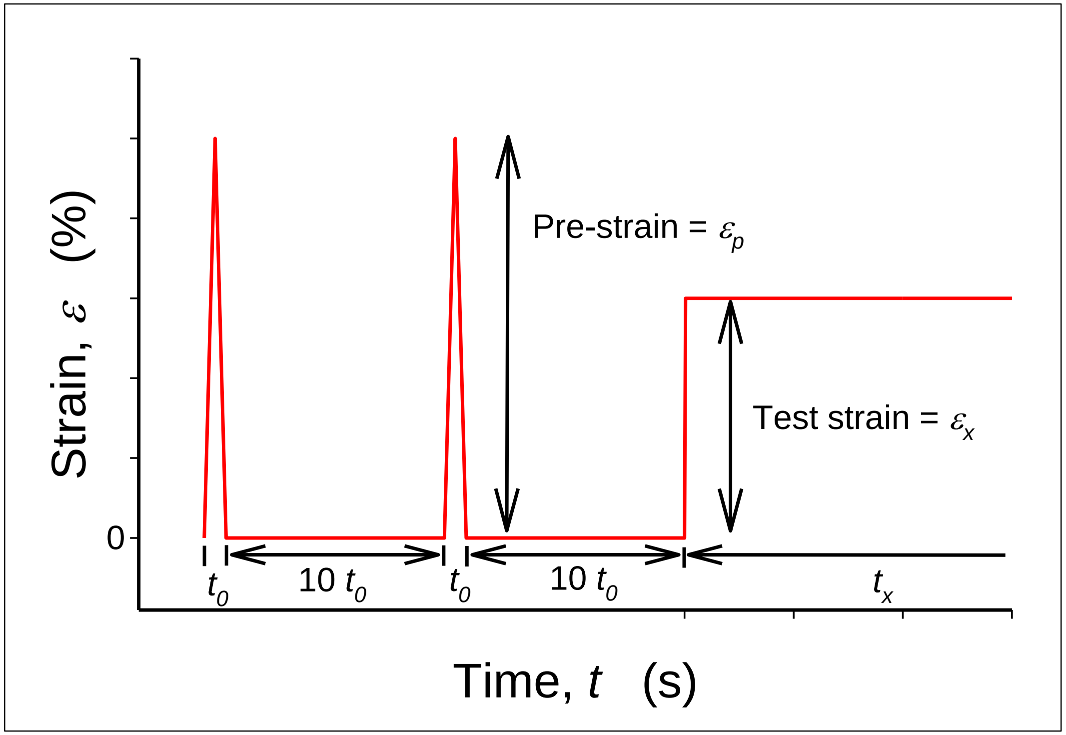
Final Test Procedure

- Pre-strain of 25 % - many sealants designed for this limit
- Test-strain levels 15 %



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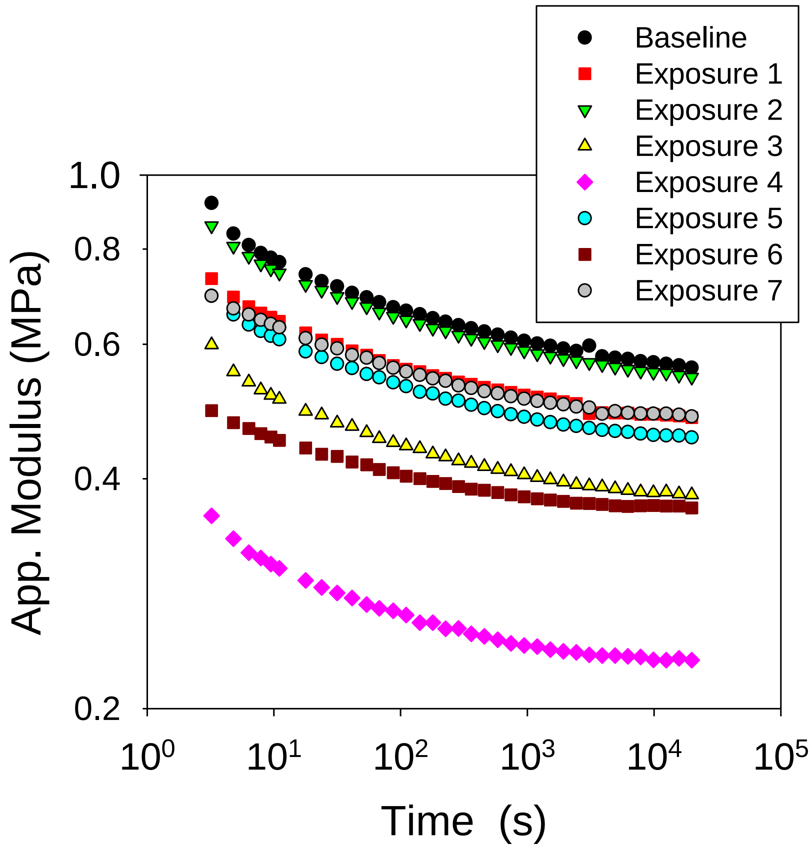
Example of Exposure Results



- Results of baseline and 7 different environmental exposures
- Exposure can change shape and vertical position of curve.
  - Shape change
    - Shift in transitions
    - Change in heterogeneity
  - Shift in vertical position
    - Change in effective cross-link density
- **Test successful for Phase 1**

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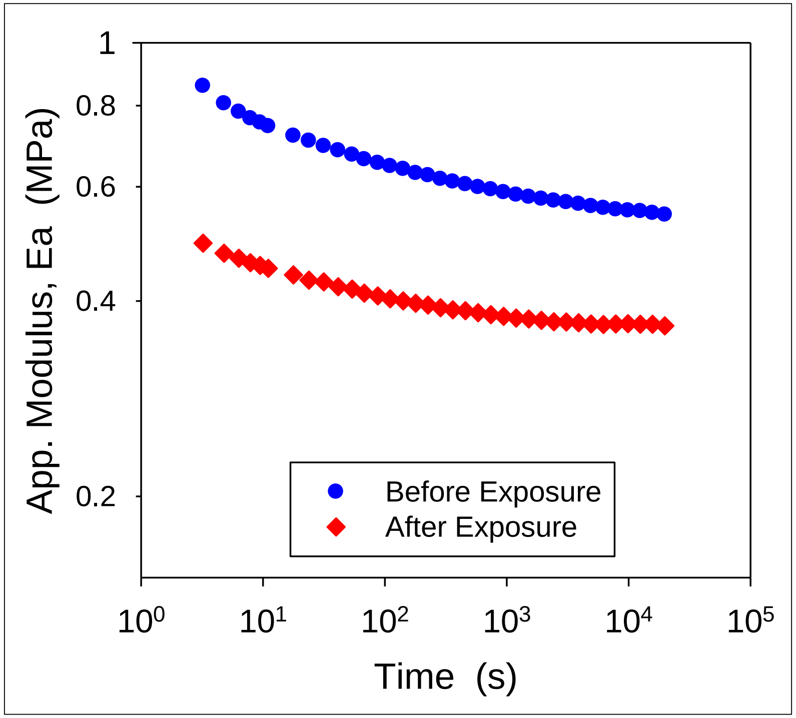
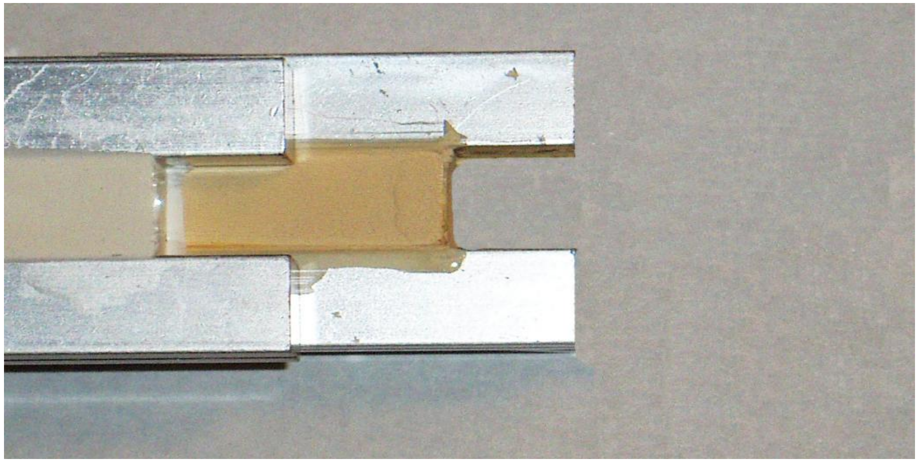
Phase 2: New Problem

- Stress relaxation at 15 % strain



- Exposure – no cracks:
  - Shift down - effective crosslink density
  - Shape – no change in glass to rubber transition



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Phase 2: New Problem

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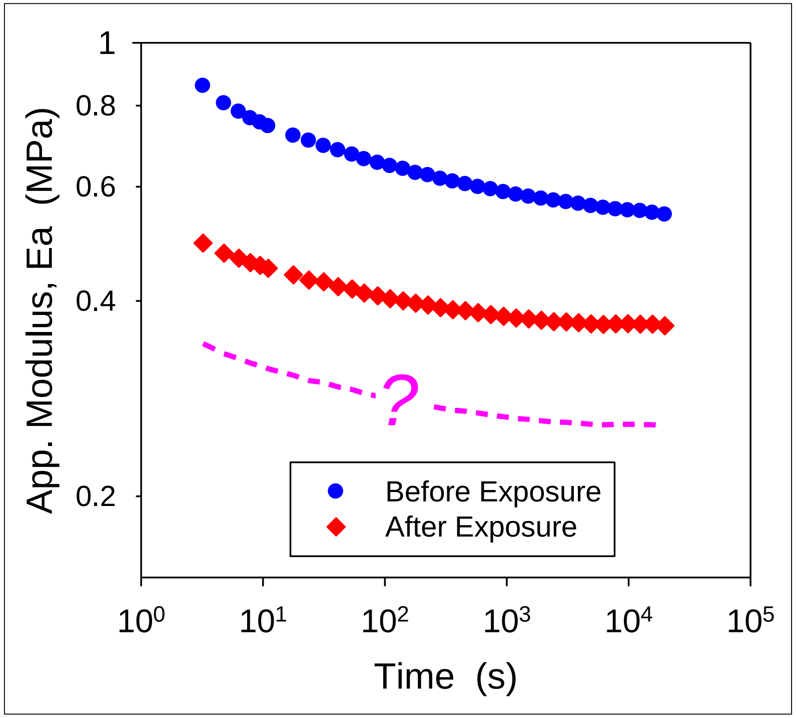
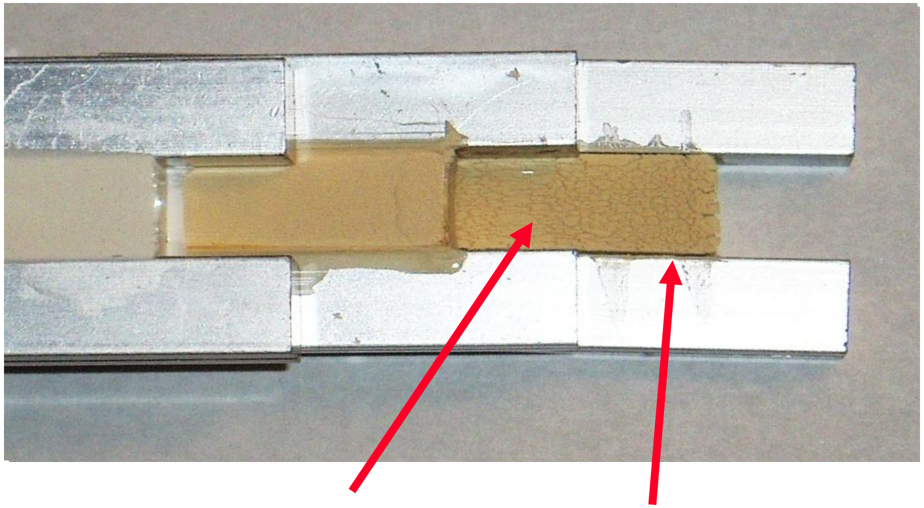


- **Interpretation is no longer straight forward**

- Exposure – no cracks:
  - Shift down - effective crosslink density
  - Shape – no change in glass to rubber transition
- More Exposure – cracks



Surface cracks

Debonds

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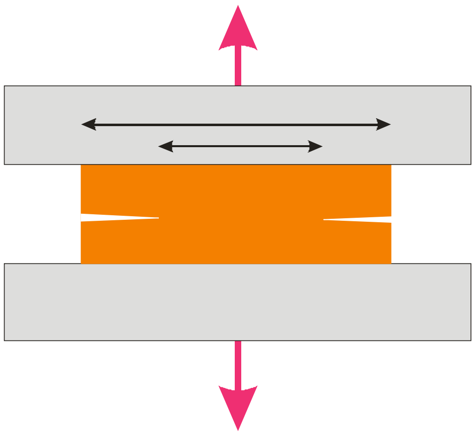
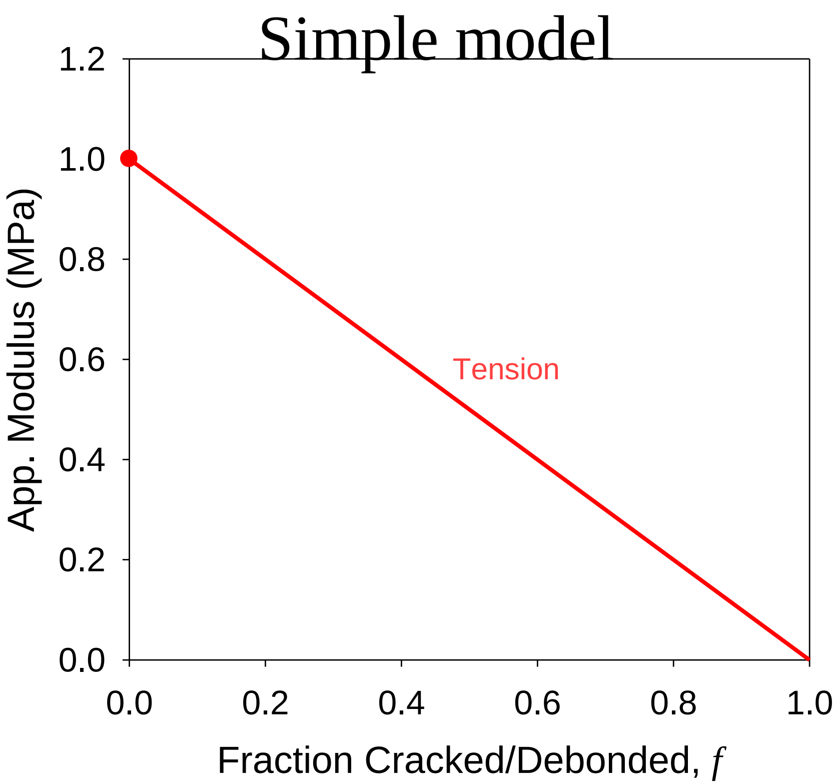
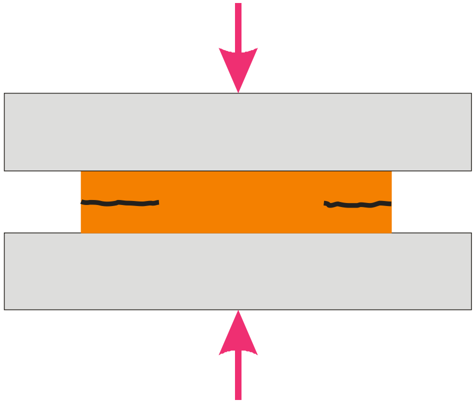
Key Idea



- Tensile load on cracked sample opens cracks
  - Reduced effective cross section lowering apparent modulus no change in time dependence
  - *f* represents fraction of cross section area that is cracked or debonded



Key Idea



- Tensile load on cracked sample opens cracks
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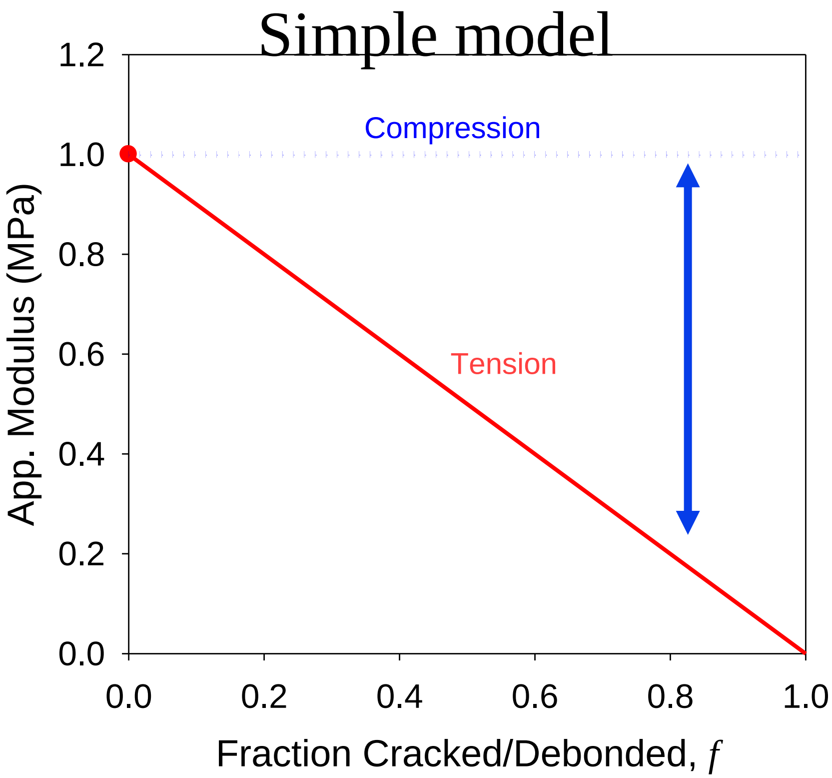

- Compression loading closed cracks so little effect on apparent modulus
- Key Idea: Use the difference between the two moduli to estimate the effective cross section – characterize cracking

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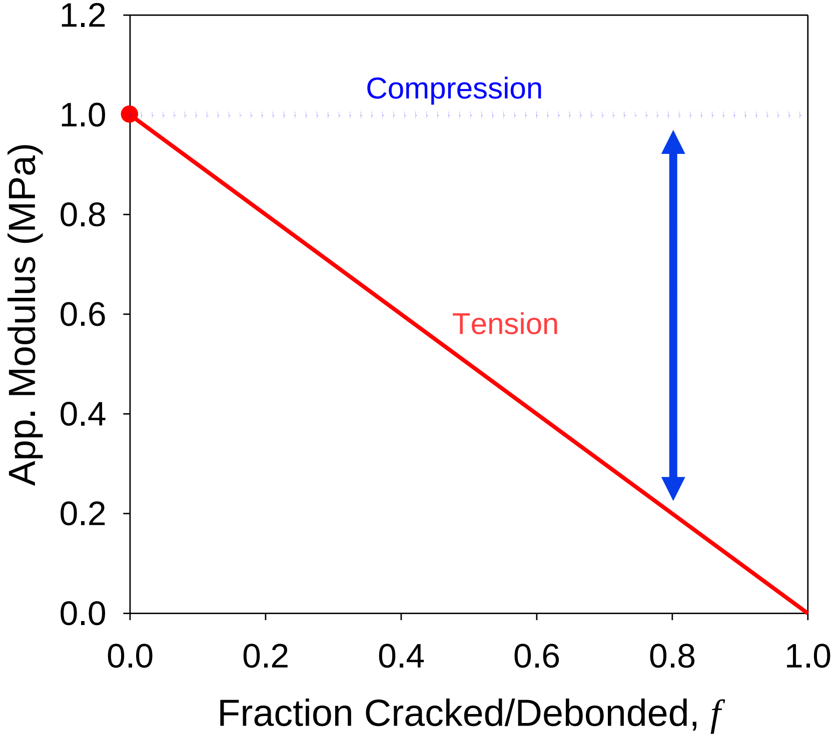
Model Development

Simple model



- Simple model but need to develop true relationships
- Two approaches
  - Insert cracks of know size and test
  - Use simple FEA calculations

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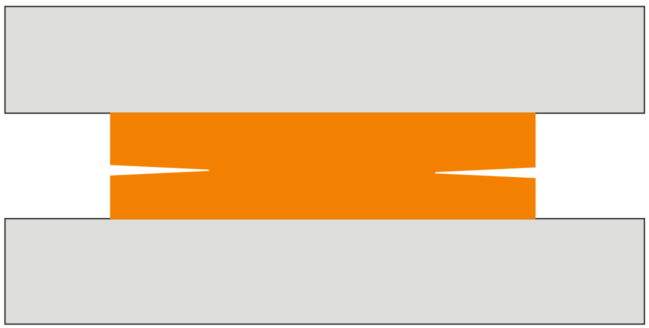
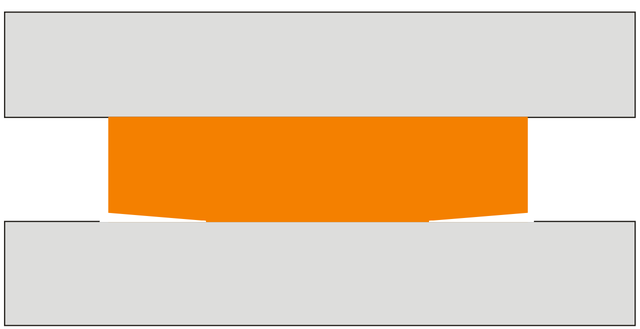
Tests with known cracks

Two crack locations





- Insert cracks or debonds with a razor blade (sealant 1)
- Crack position
  - Center of sealant (crack)
  - Interface (debond)
- Field exposure with sealant 2 tends to give interface debonds but other sealants may differ
- Vary effective cross section, fraction cracked or debonded, *f*, goes from 0 to 1

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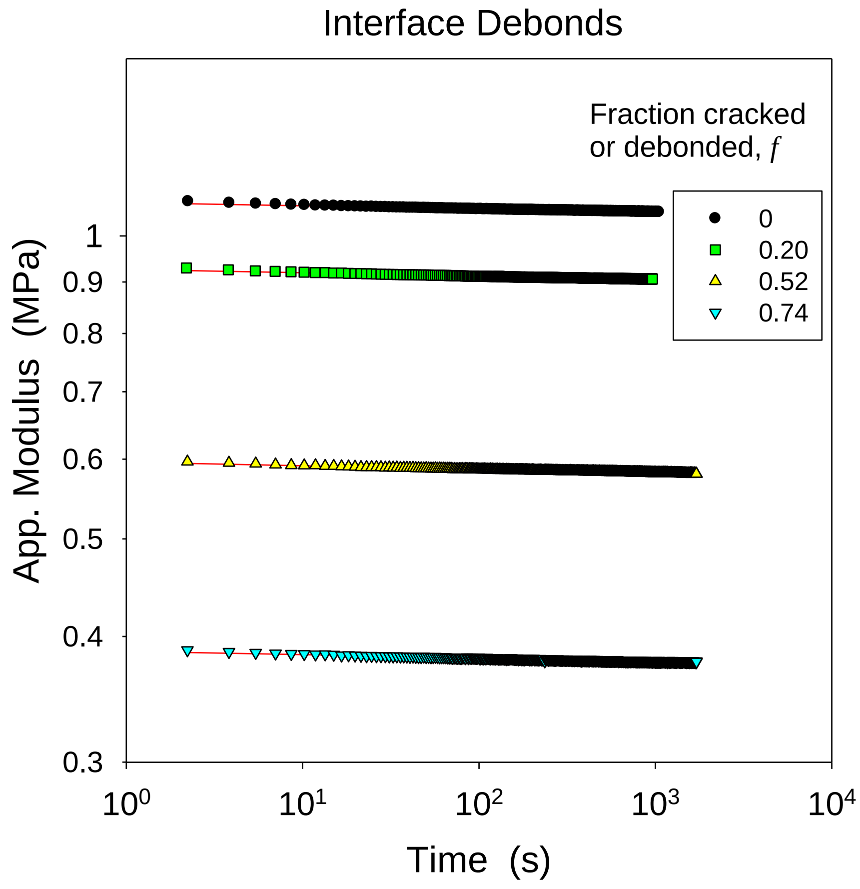
Experimental Results

- Typical results for cracked samples (sealant 1)



- All results can be modeled by power law

$$E_a = E_{100}(t/100)^m$$

  - *m* describes curve shape (in this case the slope)
  - E_{100} indicates vertical position

- As expected, cracks produce vertical shift but no change in shape (m is constant)

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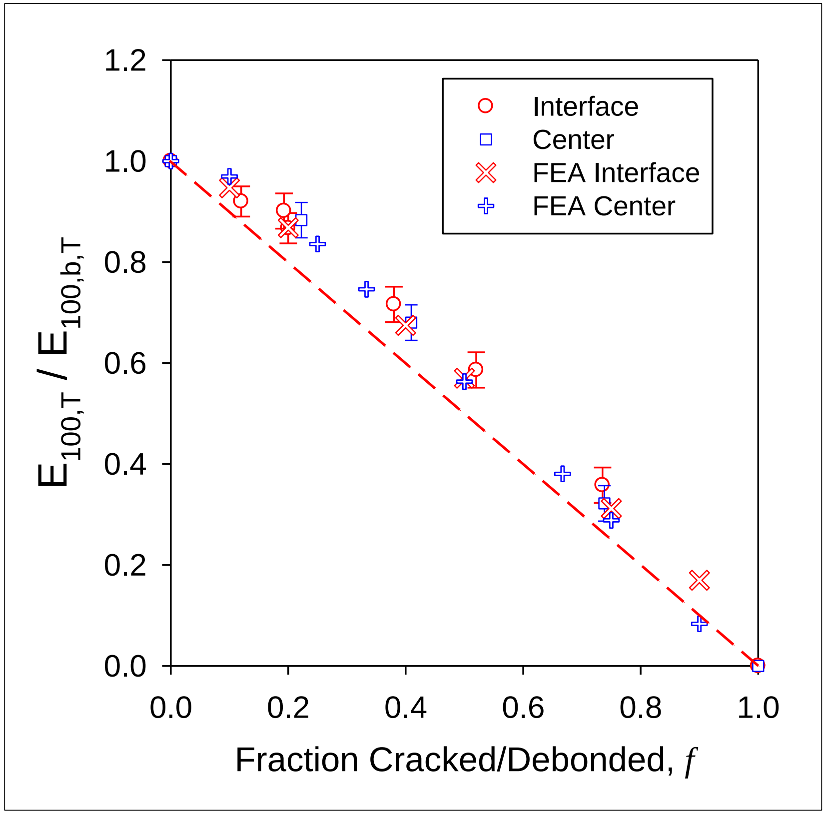
Tensile Test Results

Use ratio to normalize to 1



- Simple prediction
- Data slightly above simple prediction
- Center and interface cracks are the same
- FEA predictions consistent with experimental results

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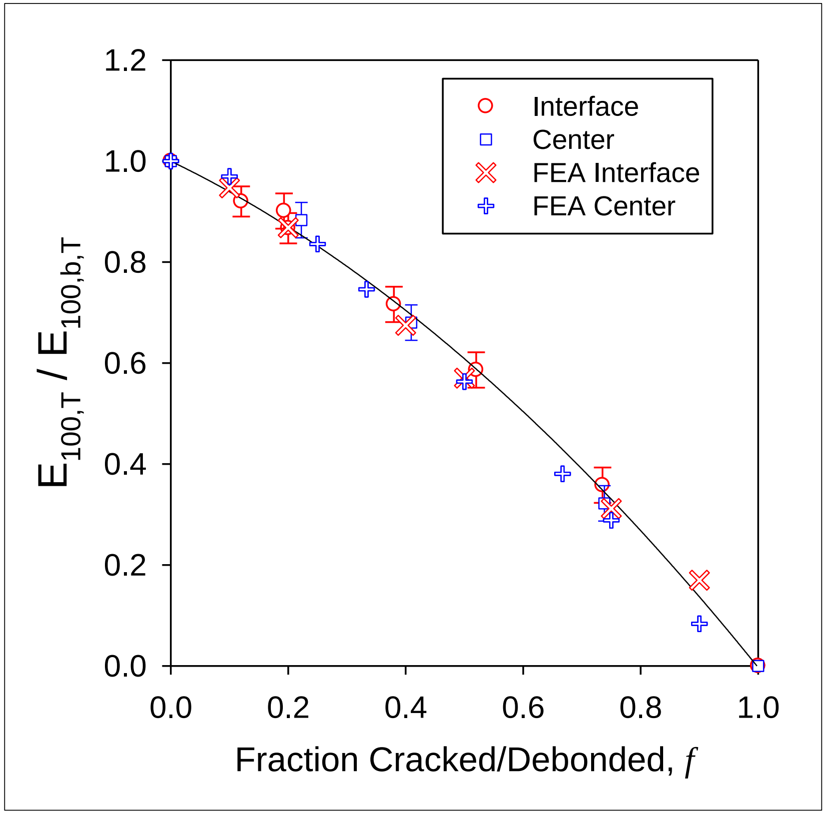
Tensile Test Results

Use ratio to normalize to 1



- Simple prediction
- Data slightly above simple prediction
- Center and interface cracks are the same
- FEA predictions consistent with experimental results
- Can model results with simple empirical equation (a_2 is a fit parameters)

$$E_{100,T} = E_{100,b,T}\left\{1 - a_2 f - (1 - a_2) f^2\right\}$$

Subscripts: *T* for tension and *b* for baseline (no cracks/debonds)

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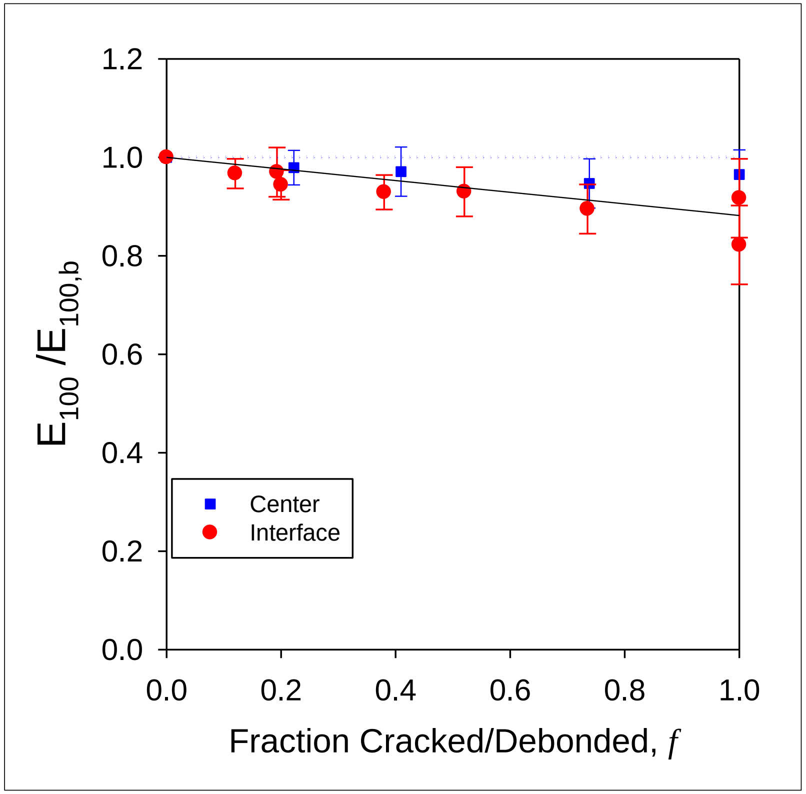
Compression Test Results

Use ratio to normalize to 1



- Data fall slightly below simple theory
- Results fit with one parameter, a_1, line

$$E_{100,C} = E_{100,b,C}(1 - a_1 f)$$

- FEA results depend on assumption about slip between crack faces

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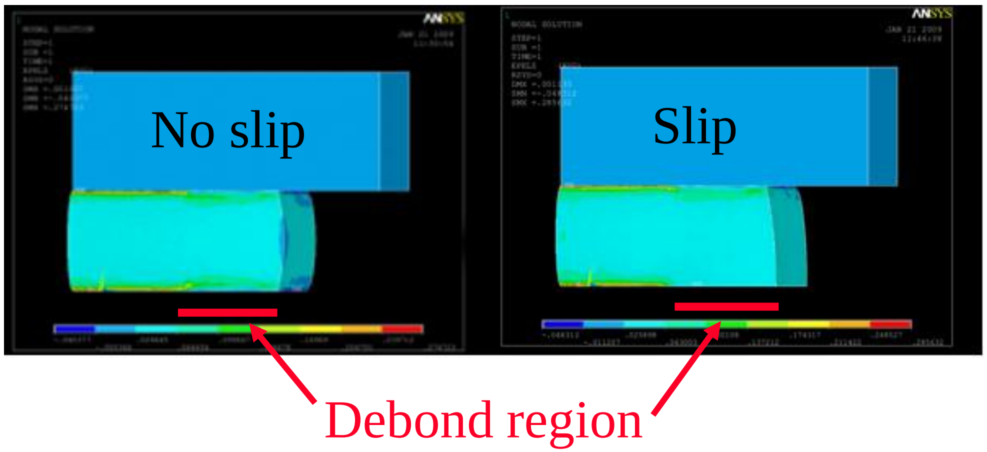
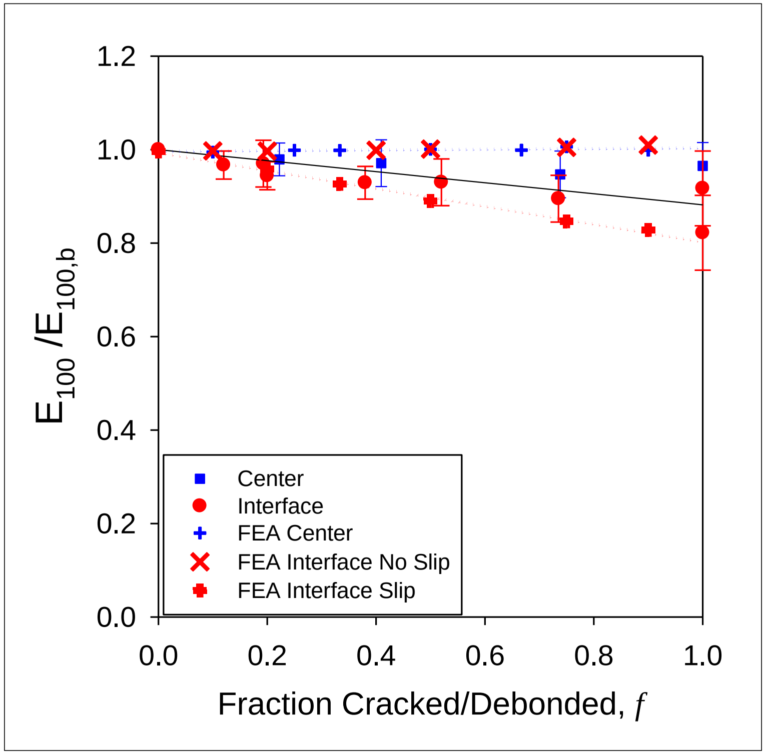
Interface Cracks

- Interface crack releases lateral constrain – consider FEA results





- FEA analysis with two extremes: Full slip at interface & no slip at interface

Experimental results between two predictions

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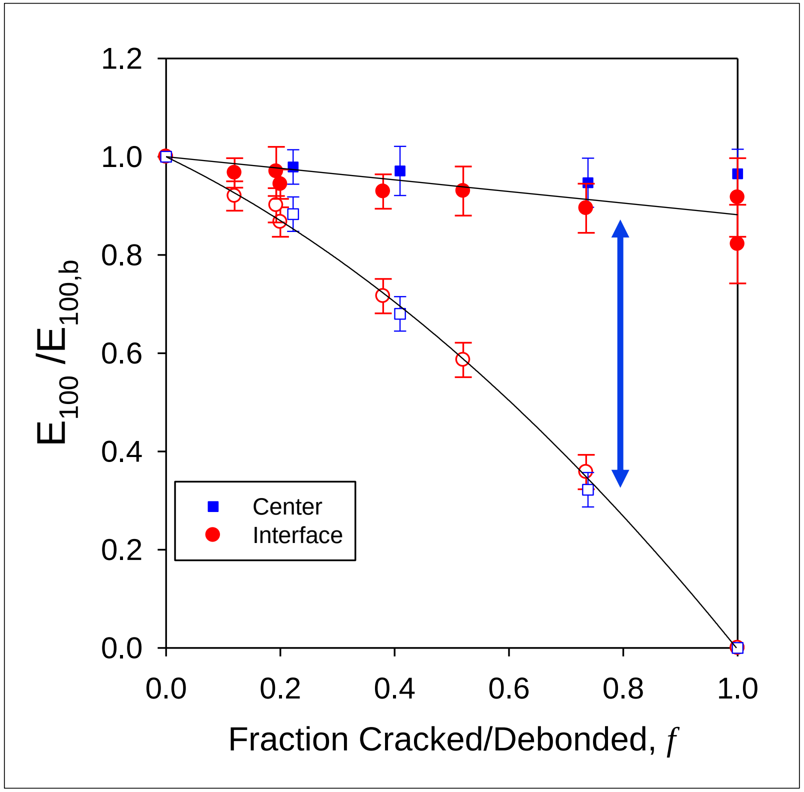
Crack Model



- Only two fit parameters a_1 and a_2

$$E_{100,T} = E_{100,b,T}\left\{1 - a_2 f - (1 - a_2 f^2\right\}$$

$$E_{100,C} = E_{100,b,C}(1 - a_1 f)$$

- Cracks/debonds: Difference in modulus ratios allows estimation of *f*
- Uncertainty
  - *f* must be > 0.15 (15 %)
  - Otherwise uncertainty in f is ±0.07 (7 %)
- Assume primarily a geometry effect so: Same a_1 an a_2 for other sealants

- Extend Model to include molecular level changes ?

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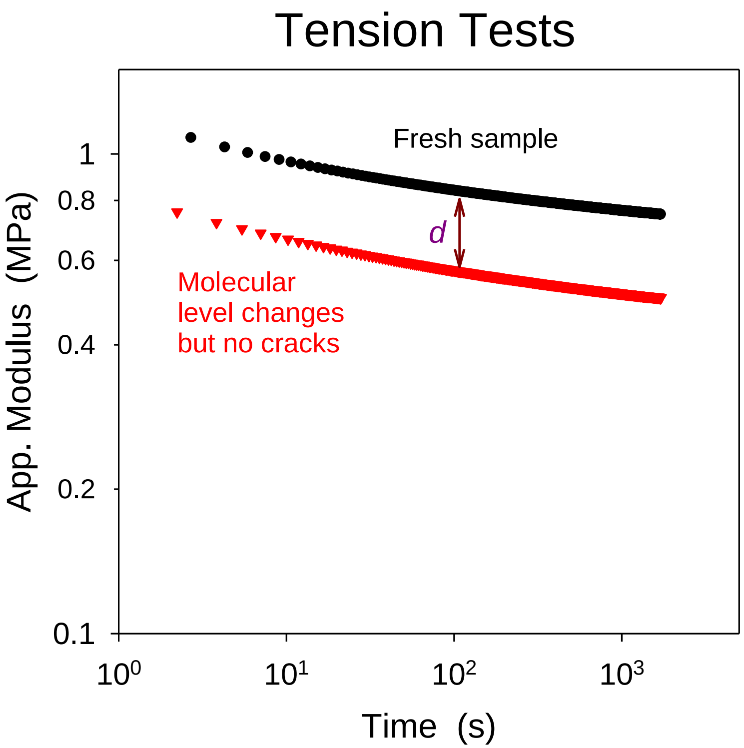
Molecular Change Model

- Curve shape change - Molecular level changes
- Vertical shift – Molecular and/or macroscopic level changes
  - Separate contribution of each



- Let *d* represent contribution to vertical shift on log-log plot from molecular change

$$E_{100,b} = d \cdot E_{100,bo}$$

  - $E_{100,bo}$ is value for fresh sample

- Assume *d* is same in tension and compression

$$E_{100,T} = d \cdot E_{100,bo,T} \left\{1 - a_2 f - (1 - a_2) f^2\right\}$$

$$E_{100,C} = d \cdot E_{100,bo,C} (1 - a_1 f)$$

- Measure quantities in blue and determine *d* and *f*

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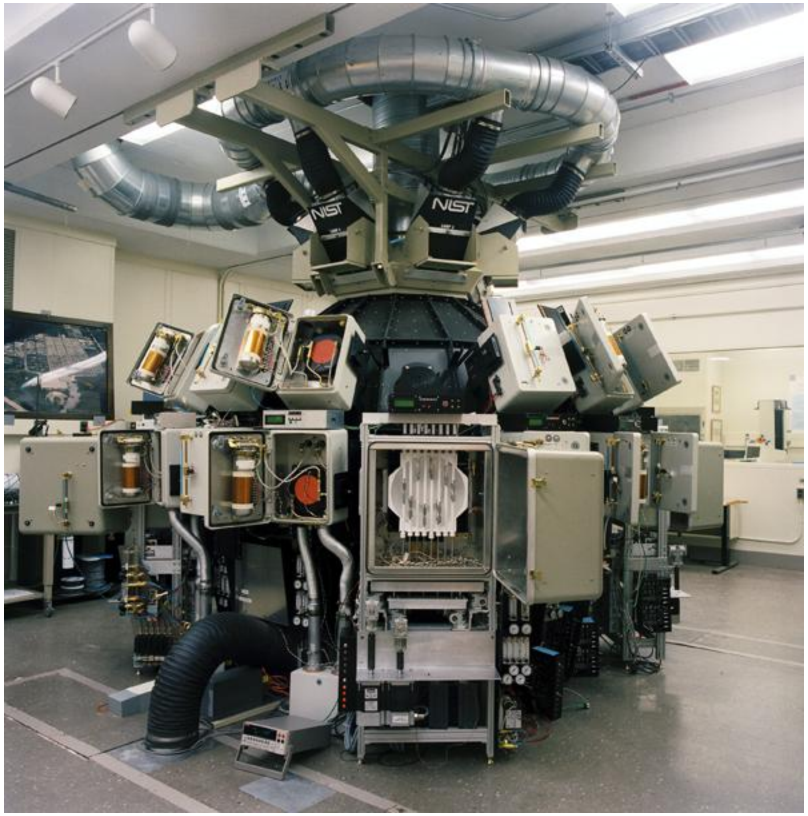
Exposure Tests



- Sealant 2
- Exposure: 1 month in SPHERE
  - UV: ≈ 2 years continuous sunshine
  - Motion: Triangular wave between strains of 0 % and 25 % with period of 30 min.
  - Relative Humidity: 25 %
- Condition 1 – above at 30 °C
- Condition 2 – above at 50 °C
- Specimens
  - 2 no exposure
  - 3 exposed at condition 1
  - 2 exposed at condition 2

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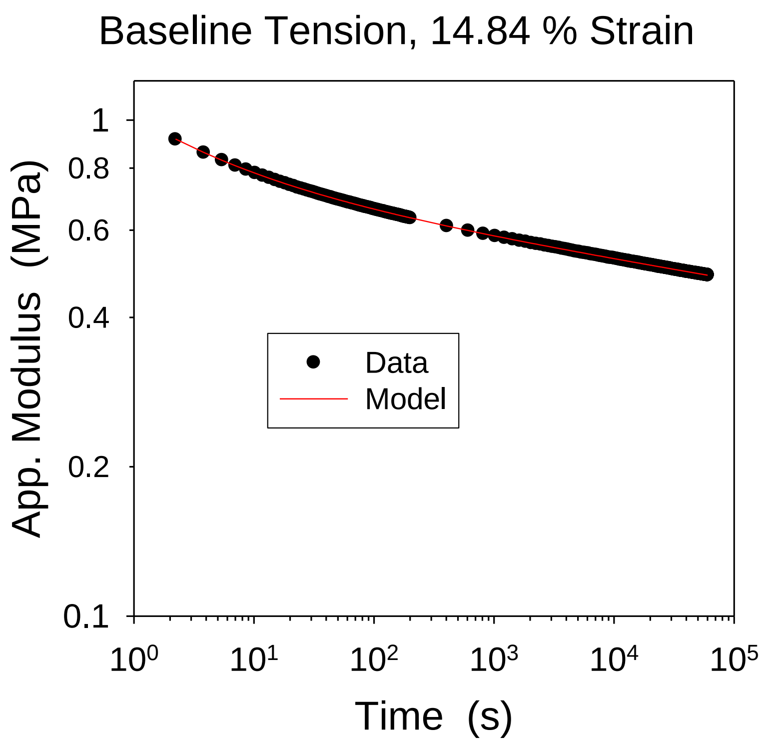
Results for Exposed Specimens

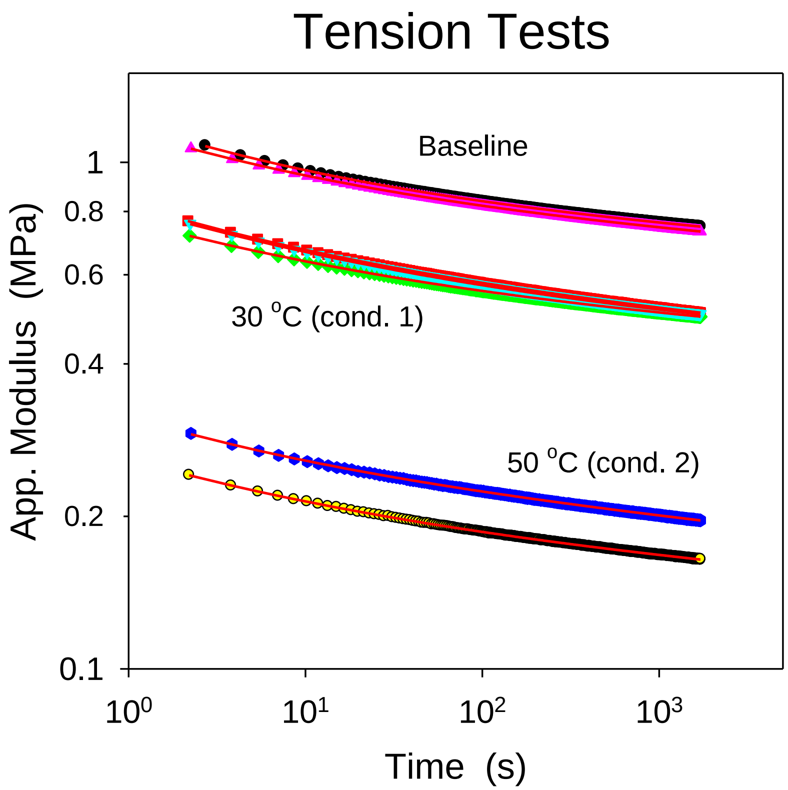


- Results show significant curvature for sealant 2 so modeled with

$$E_a = E_{100}(t/100)^m \left\{1+(t_s/t)^n\right\}$$

  - Fit parameters
    - » m, n, t_s – curve shape
    - » E_{100} vertical position

Results for Exposed Specimens



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  - Fit parameters
    - » m, n, t_s – curve shape
    - » E_{100} vertical position

- Exposured curves – change in E_{100} only
- Compression curves similar but smaller shifts in E_{100}

- Use E_{100} values from tension and compression to calculate molecular and macro level changes

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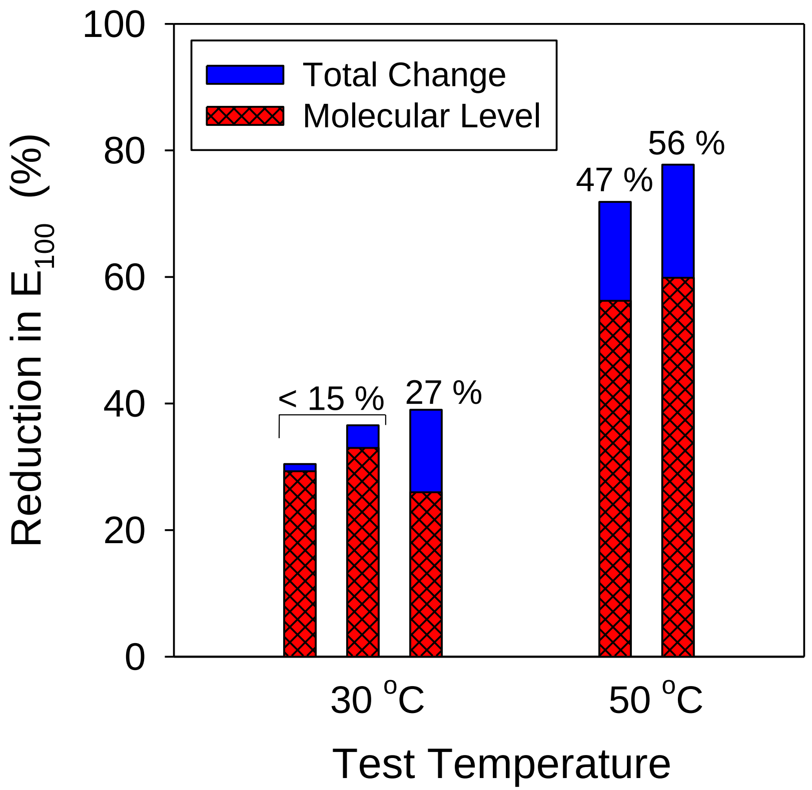
Predictions from Experiments

Fraction of cross section cracked or debonded show above bars



- Total reduction in E_{100} is separated into components from molecular and macroscopic effects
- 2 of 3 samples exposed at 30 °C predict no cracking
- Both specimens exposed at 50 °C predicted to show significant cracking.
- Verify calculations ?
  - 3 tests

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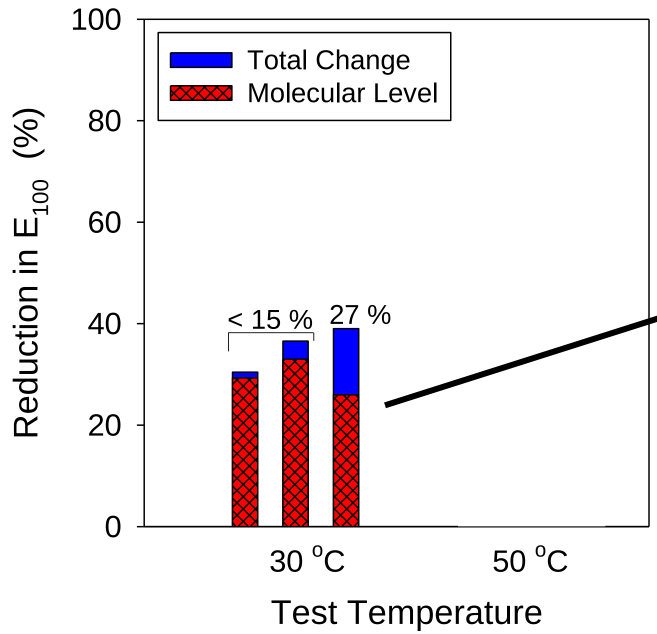
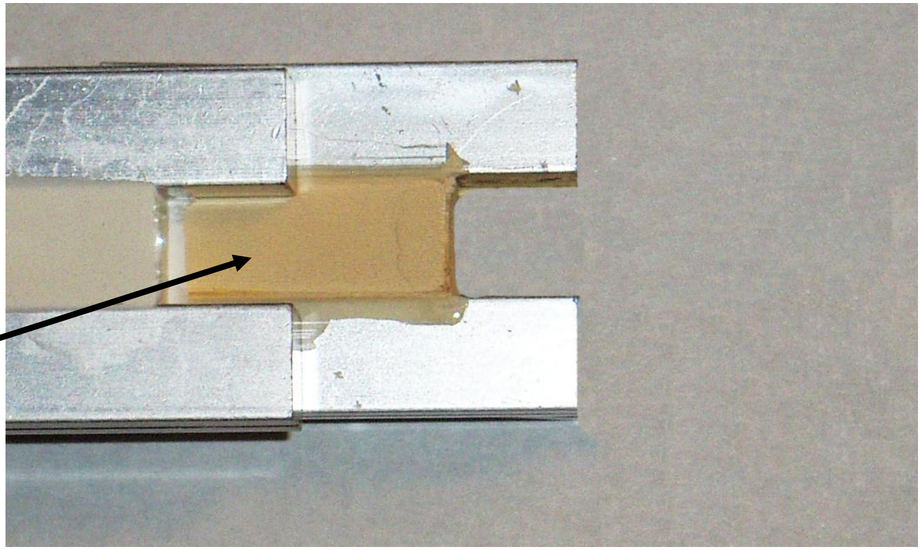
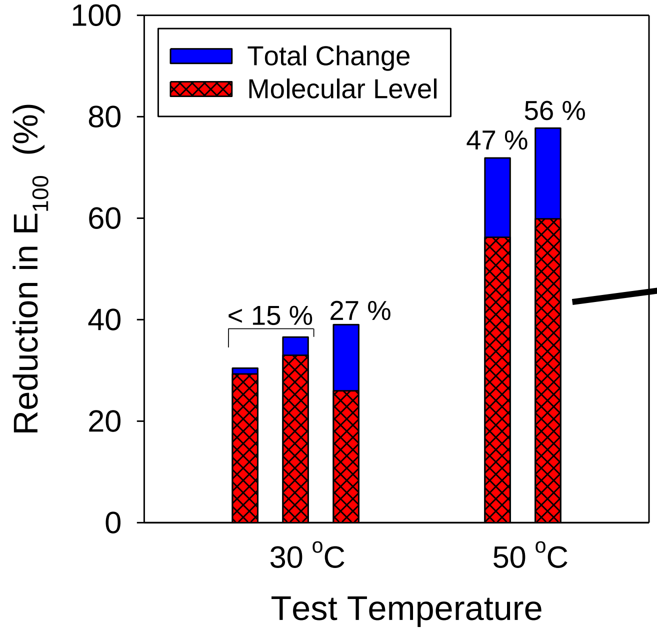
Test 1: Visual Observations

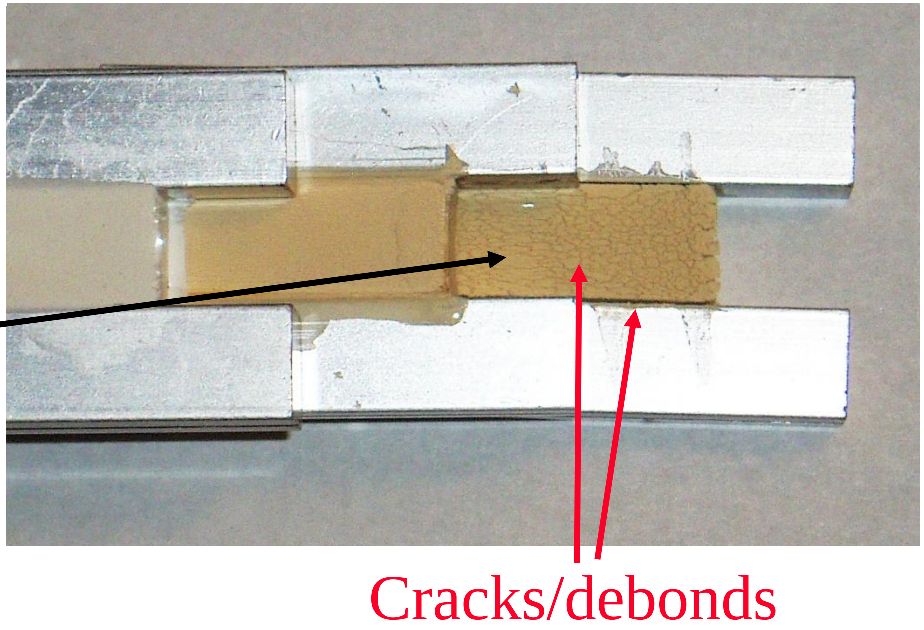




- Specimens exposed at 30 °C show color change but little or no cracking in 2 out of 3 cases

Test 1: Visual Observations





- Specimens exposed at 30 °C show color change but little or no cracking in 2 out of 3 cases
- Specimens exposed at 50 °C show minor surface cracking and significant debonding

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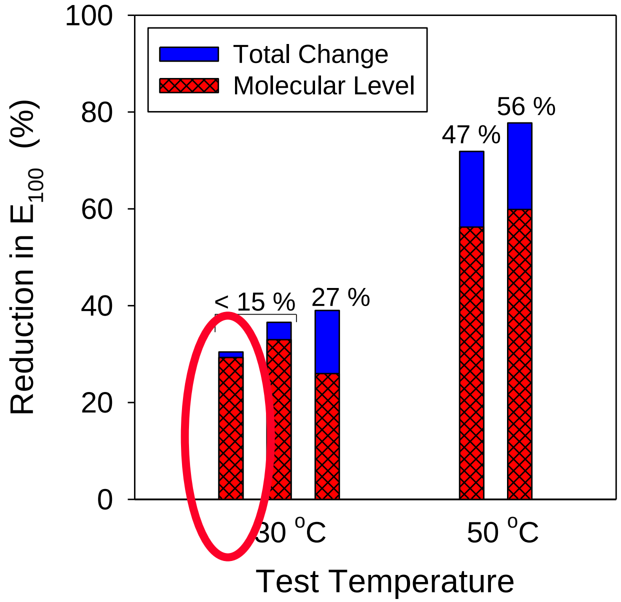
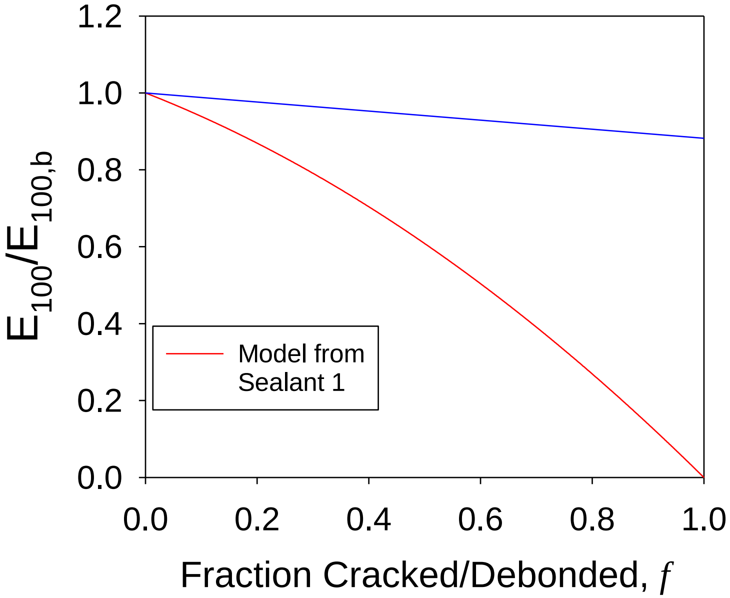
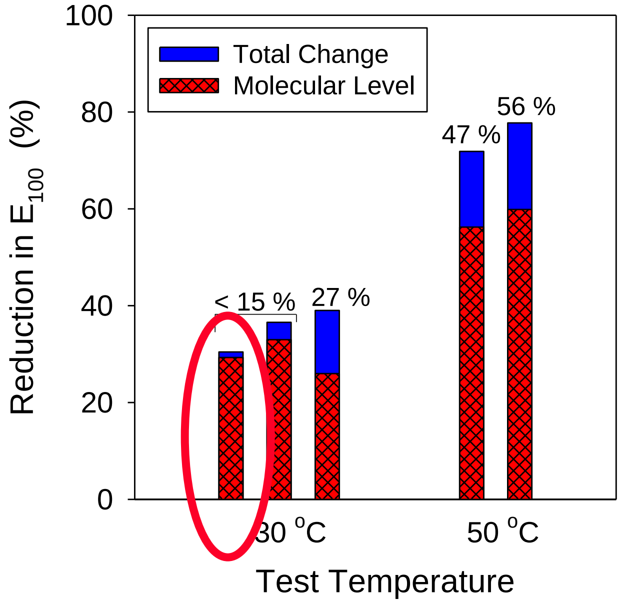
Test 2: Insert Known Cracks

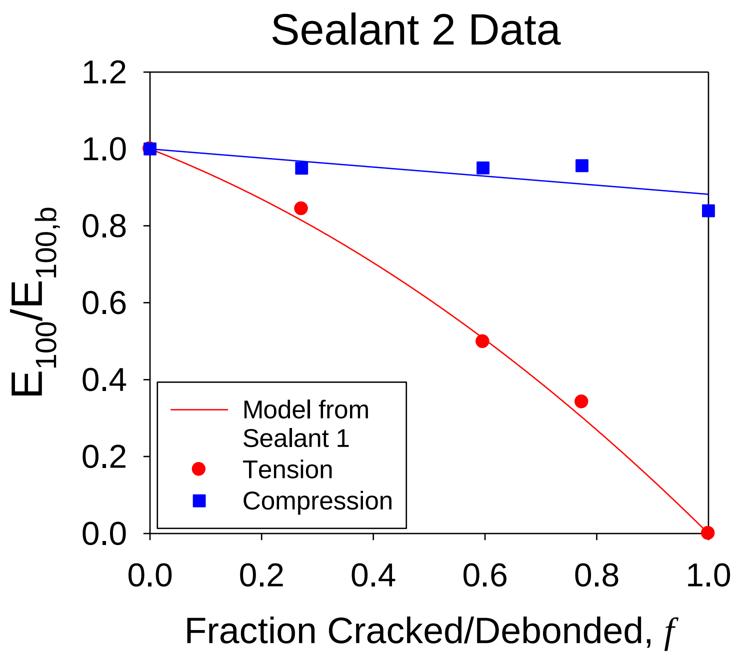




- Razor debonds in exposed but uncracked specimens

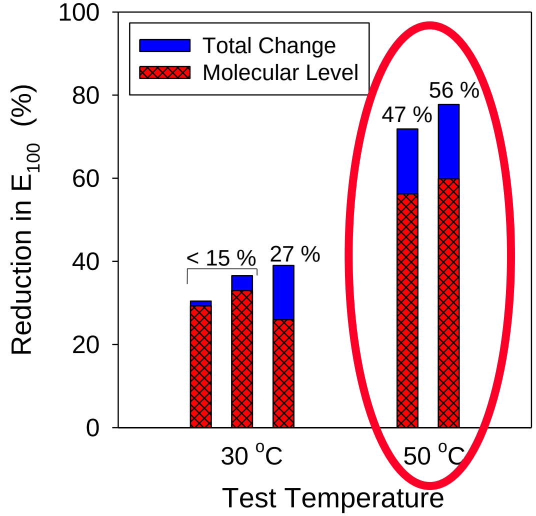
Test 2: Insert Known Cracks

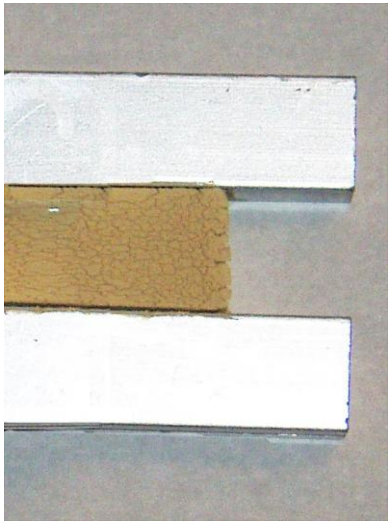


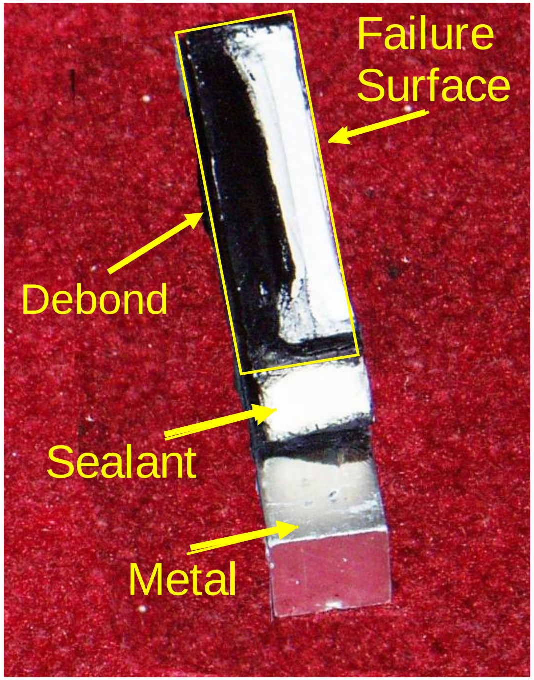


- Razor debonds in exposed but uncracked specimens
- Data (points) in good agreement with curves from experiments on sealant 1

Test 3: Measure Cracks







- Examine samples where cracks are predicted
- Coat cracks with ink, let dry, and pull to failure.
- Cracked areas on failure surface coated with ink – use image analysis to determine f

Sample	*f* from modulus ration	*f* from image analysis
1	(47 ± 7) %	(52 ± 5) %
2	(56 ± 7) %	(60 ± 5) %

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Conclusions

- Only a few results so far but the technique looks promising
  - For model system, method seems to provide good estimations for changes on both molecular and macroscopic levels
  - Non-destructive and potential to perform without removing sample from chamber
- Additional test required to validate test
  - Different cracking geometries (model development)
  - More data for exposed samples
  - Different sealant materials

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