Kinetics Based Models to Describe Environmental Degradation of Polymeric Sealants

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Introduction

Background – Previous Results

Model Development

Experiments and Model Testing

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Introduction

- What is a sealant ?
  - Elastomer used to prevent air & moisture intrusion into a structure
  - Structural function as well

  - Widely used throughout most structures (buildings, cars, etc.)
  - 30 billion dollar a year industry
  - 420,000 tons produced per year

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Challenge

- ❑ 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

- ❑ 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

- ❑ **Critical Need – Good durability tests & predictive models**
  - – **Anticipate repair**
  - – **Improve materials**

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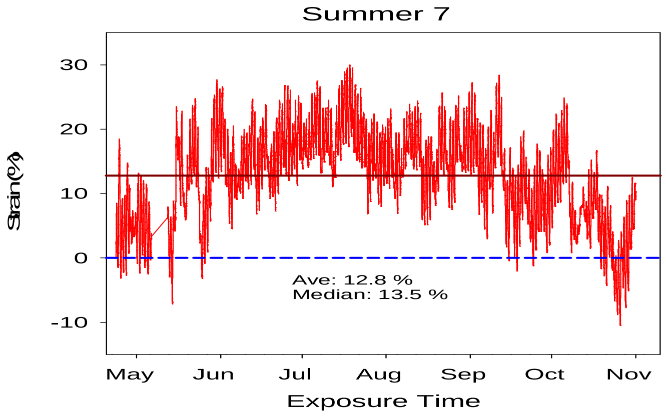
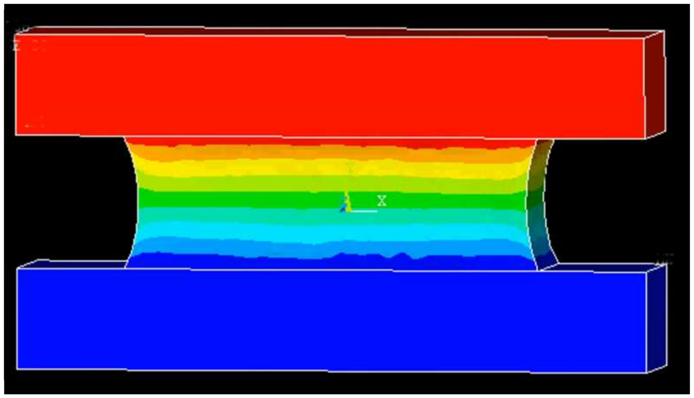
Background – Previous Results

- **NIST initiated a consortium with a number of sealant suppliers and other laboratories to address this issue**

- Potential variables
  - Temperature
  - Light (UV radiation)
  - Humidity
  - Strain



- 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

$$E_a = S\ E$$

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Metrology

- Two approaches to exposure

- Outdoor Aging

  - Realistic but
  - Time consuming
  - Uncontrolled and never get same conditions twice – complicates modelling and prediction

- Laboratory Aging
  - Can control variables
  - Add dynamic strain control
  - Potential to accelerate
  - Must relate to real life

- Ultimate goal: Use accelerated lab data and models to predict outdoor behavior

- **Initial focus: Formulate models to fit lab data and use models to predict other lab results**

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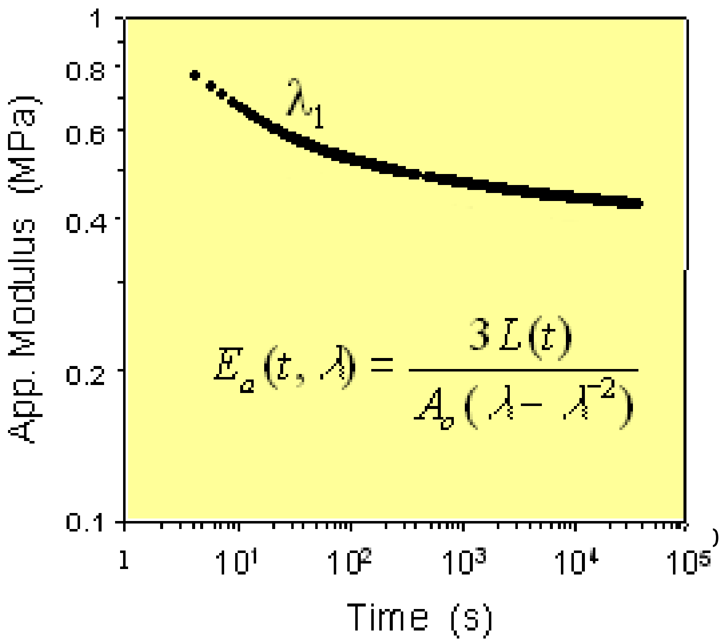
Program Procedure

- Test procedure
  - Characterize fresh sample (laboratory conditions)
  - Subject to exposure
  - Extract and re-characterize (lab conditions)
  - Repeat last 2 steps
  - Result: Behavior vs exposure time
- Characterization method based on mechanical properties
  - Not material dependent
  - Mech. properties important
  - Challenge sealants are non-linear viscoelastic materials
  - Stress relaxation experiment (ASTM C1735-11)



- Use theory of rubber elasticity to determine the apparent modulus curve

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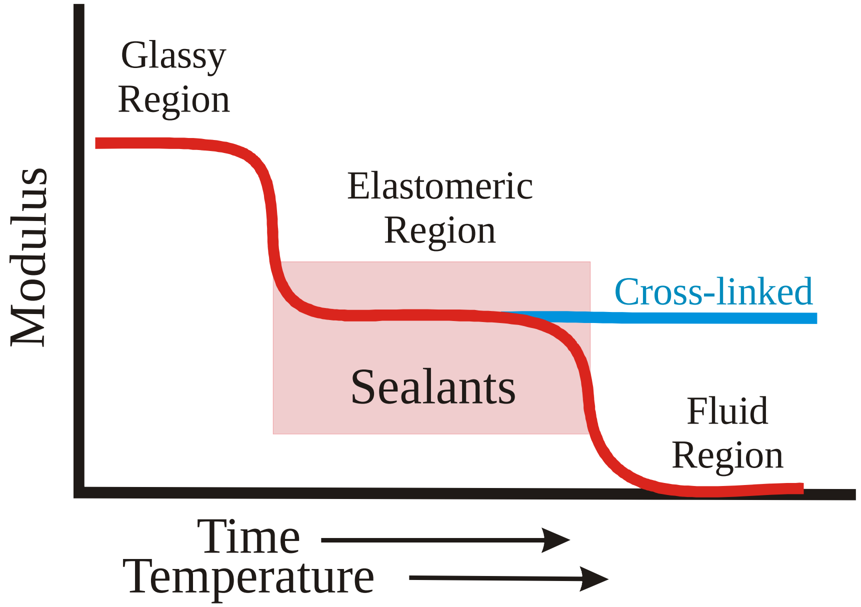
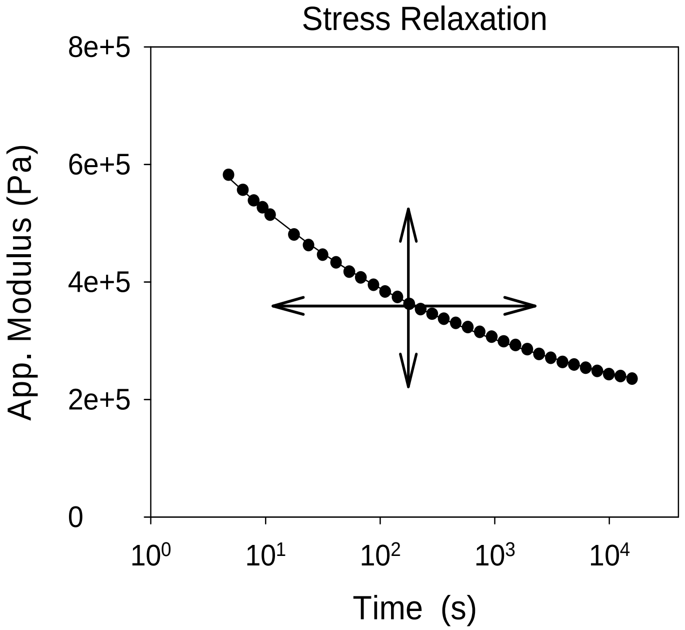
Sealant Behavior

- Sealants are elastomer so stress relaxation test provides indicated part of curve
- Monitoring how this curve is changed by exposure can tell us something about what is happening on a molecular level.





- Curve can (1) change shape, (2) shift horizontally, or (3) shift vertically

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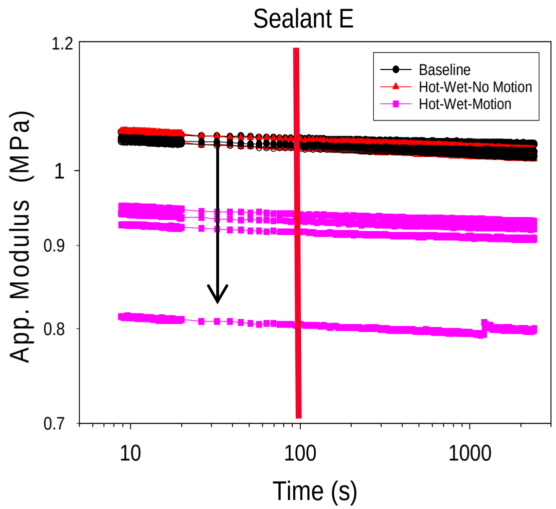
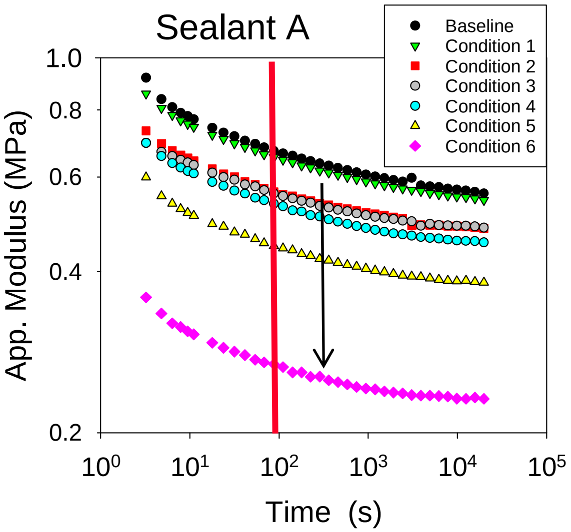
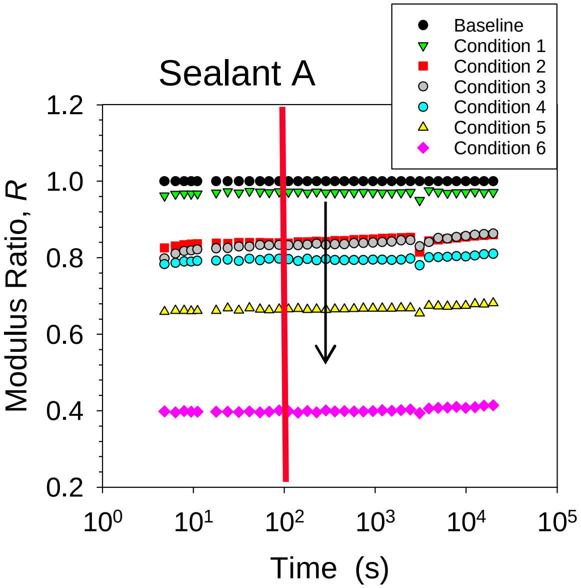
Previous Results

- Tests on 18 different sealants, 9 have shown environmentally induced changes to date. We learn 4 things.
  - First: For 8 of the 9 the dominant change was a downward shift in the curve with little or not change in shape.







  - Behavior often similar despite the wide range of chemistry, formulations, and test conditions used.
  - Second: Some surface changes but no evidence of serious cracks and debonds until late in the process so changes are probably at a molecular level until near the end.
  - Third: Measure of degradation is $\boldsymbol{R = E/E_o}$ where E_o is the initial curve for fresh sample. Vertical shift produces horizontal straight line for $R(t)$ vs t.
  - Fourth: Since vertical position is important parameter, changes can be characterized by value, R, at fixed test time, say 100 s.

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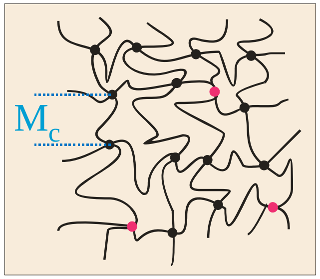
Model Development

- E represents the rubbery plateau modulus
- Ideal network $E = \frac{3RT}{2}\alpha$ where α is cross-link density.
- Sealants are far from an ideal network. Their networks have affective cross-link or junction points
  - Chemical links
  - Chemical and physical attachments to fillers
  - Crystalline regions
  - Rigid blocks in block co-polymers
  - Etc.



- Nevertheless, reasonable assumption that modulus is proportional to density of affective junction points, α

$$E = C\,\alpha$$

- Environmental degradation then proceeds by a reduction in α until cracks for late in the process.

Equations

- For the process prior to the formation of cracks, consider the kinetics for reduction in a which produces the decrease in E via $E = C\ \alpha$
- Consider first <u>exposure under constant or fixed environmental conditions</u>
- Two <u>simplest</u> models where rate constant, $k(T, RH, I_{UV}, \varepsilon)$, is dependent on environmental variables but not exposure time.

- Zero order kinetics

$$d\alpha / dt = -k$$

$$\alpha = \alpha_o - kt$$

$$E = E_o - [Ck]t$$

$$R = E / E_o = 1 - [Ck / E_o]t$$

- R as linear function of t
- There is limit $t < [E_o/Ck]$

- First order kinetics

$$d\alpha / dt = -k\alpha$$

$$\alpha = \alpha_o e^{-kt}$$

$$E = E_o e^{-kt}$$

$$R = E / E_o = e^{-kt}$$

- Not a linear function of t
- Plot ln(R) vs t is linear

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Additional Option

- Not all cross-links can be degraded: different types or skin effect

$$E = C\left(\alpha + \alpha_\infty\right)$$

- Zero order kinetics

$$\alpha = \alpha_o - kt$$

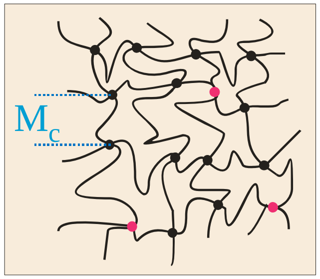
$$E = E_o - [Ck]t$$

$$R = E / E_o = 1 - \left[\frac{Ck}{E_o}\right]t$$

- Same equation but different limit

$$t < (E_o - E_\infty) / Ck$$

- First order kinetics



$$\alpha = \alpha_o e^{-kt}$$

$$E = C\alpha_o e^{-kt} + C\alpha_\infty$$

$$E = (E_o - E_\infty)e^{-kt} + E_\infty$$

$$\boxed{R = (1 - R_\infty)e^{-kt} + R_\infty}$$

- Can linearize if R_∞ is known and constant.

$$\ln\frac{R - R_\infty}{1 - R_\infty} = -kt$$

- Usually not constant

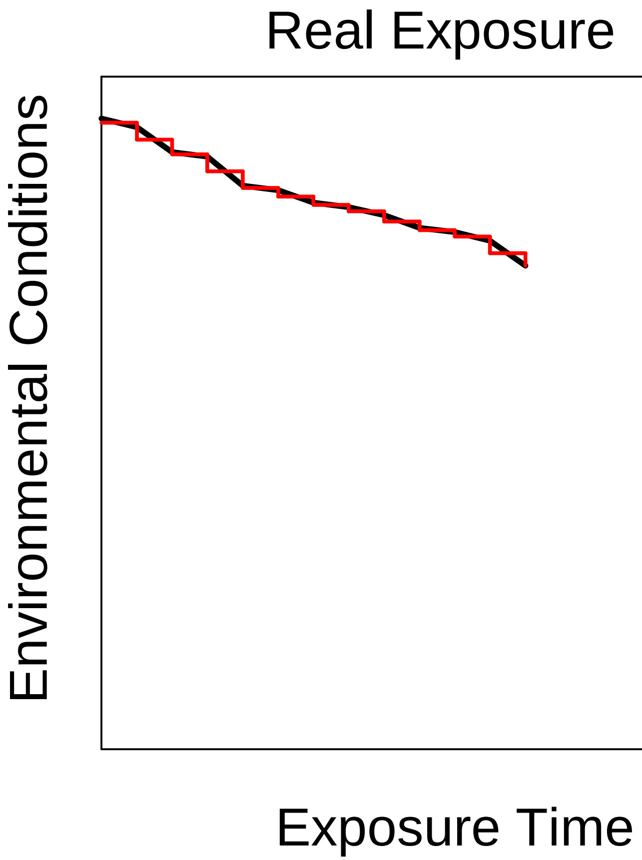
3 possible equations: *R* vs *t* is linear, ln(*R*) vs *t is* linear or fit data with equation above

Extension of Models

- Previous equations for constant conditions, but in real exposure, the conditions are constantly changing.
- Try simple damage accumulation approach
  - Approximate continuous change with steps at constant conditions (<u>environment changes slowly</u>)
  - Determine increased damage at fixed conditions during each step, ΔD_i .
  - Value of Property after exposure time t_n is

$$P(t_n) = P(0) - \sum_{i=1}^{i=n} \Delta D_i$$

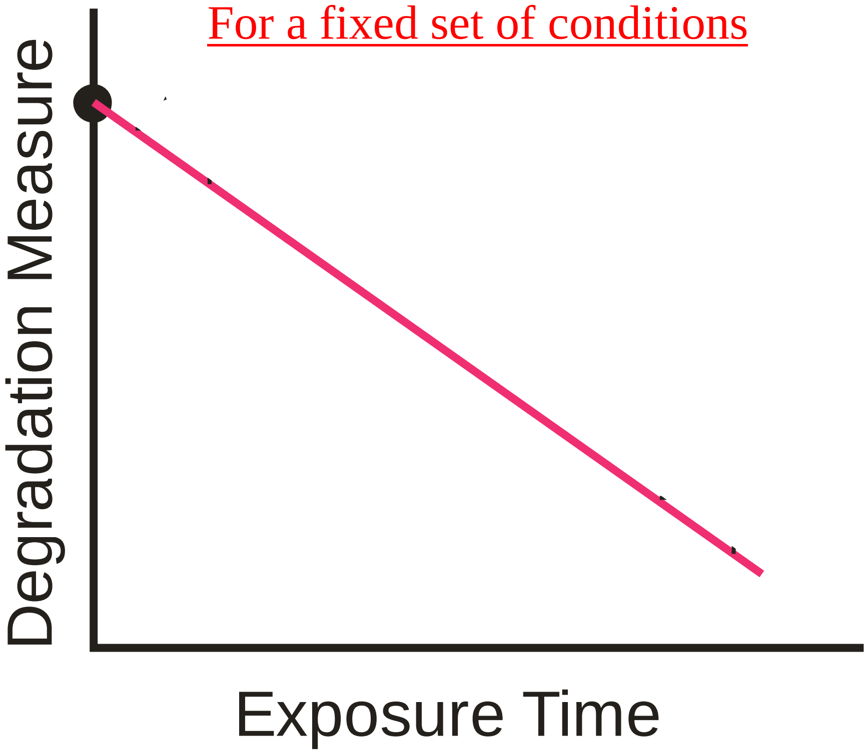
  - ΔD_i depends on environmental conditions during step and perhaps the state of the material at start of the step



- Challenge is to determine ΔD_is

Challenge

- If we can define the measure of degradation so it is a linear function of time i.e *R* or ln(*R*), process simplified
  - Damage generated in Δt is same at any point in exposure
  - Need only single parameter, slope *s*, for a given set of conditions to determine $\Delta D = s\ \Delta t$
- Easy to determine slope but not for every possible condition.
- Generate data base of slopes for wide range of conditions, then apply an interpolation scheme to estimate others condition.



- So for model we need (1) data base, (2) interpolation scheme, and (3) damage accumulation equation.

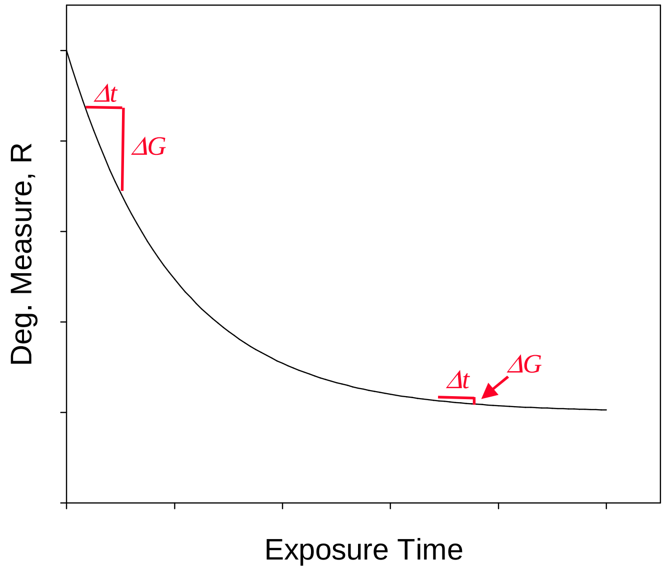
$$P(t_n) = P(0) - \sum_{i=1}^{i=n} \Delta D_i$$

If Behavior is not Linear

- If you cannot linearize equation, things are more complex.
- Example: First order with residuals

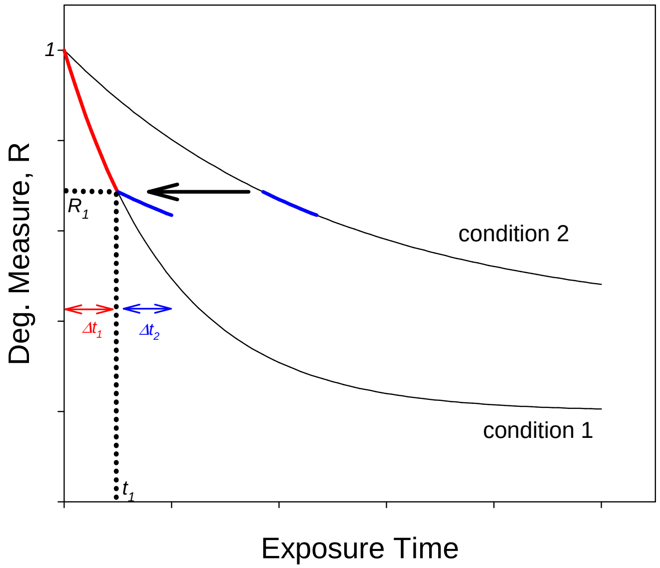
$$R = (1 - R_\infty)\, e^{-kt} + R_\infty$$

  - Can linearize if R_∞ is independent of exposure conditions.
  - This is probably not true in most cases.



- Now 2 parameters to determine for each set of environmental conditions, k & R_∞
  - We generate a data base for both k and R_∞ at a wide range of conditions.
  - We use interpolation schemes for both k and R_∞ to estimate values of parameters at environmental conditions not directly measured.
- Finally, we need a way to combine steps.

Consider Two Step Situation



- Base curves for two exposure.
- First expose at condition 1 for time, Δt_1. *Behavior follows red curve and.*

$$R = (1 - R_{1\infty})e^{-k_1 t} + R_{1\infty}$$

- At the end of step 1 value of $R=R_1$ & $t=t_1$: $t_1 = \Delta t_1$

$$R_1 = (1 - R_{1\infty})e^{-k_1 t_1} + R_{1\infty}$$

- Now in second step, exposure changes to condition 2 for Δt_2

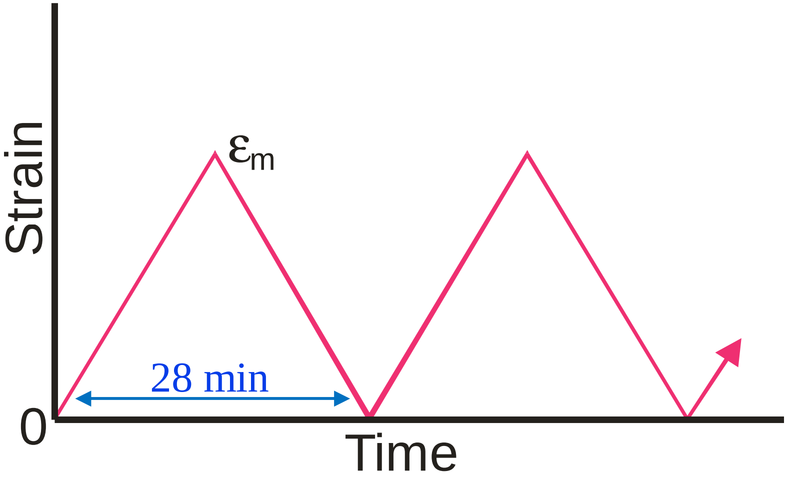
$$R = (1 - R_{2\infty})e^{-k_2 (t_s + t - t_1)} + R_{2\infty}$$

- Can be rearranged to give $$R = (R_1 - R_{2\infty})e^{-k_2 (t - t_1)} + R_{2\infty}$$

Can be generalized: Behavior in step, *i*, depends on the parameters k_i and $R_{i\infty}$ and the end position of previous step $R_{(i-1)}$ and $t_{(i-1)}$

Experiments and Model Testing

- Examine these models with Laboratory Aging data
- Need results where we have clear change in properties and most exposure time data.
- Kraton-D (styrene-butadiene-styrene tri-block polymer)
  - Displays the properties of a sealant
  - Contains double bonds sensitive to oxidation so quicker degradation.
- Tests
  - Relative humidity 50 %
  - UV Radiation 50 W/m^2
  - Temperatures: 21 C, 31 C, 41 C, or 51 C
  - Fixed strain history: ε_m = 0 %, 11 %, or 21 %



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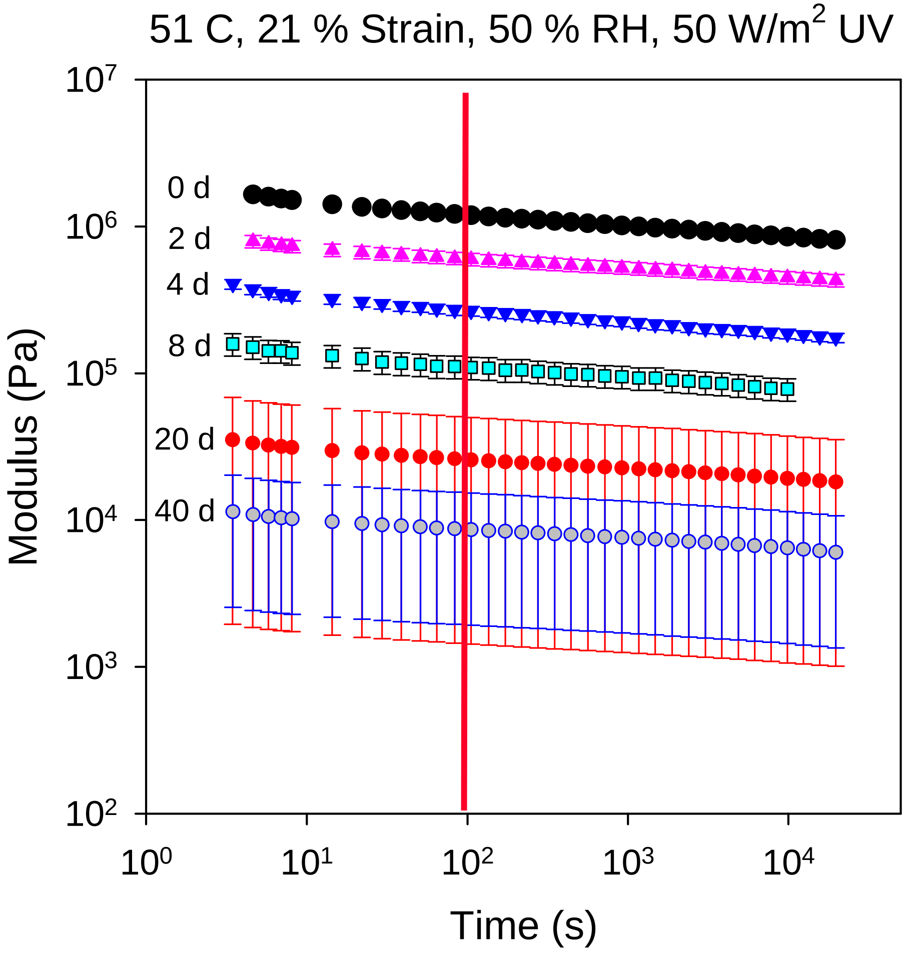
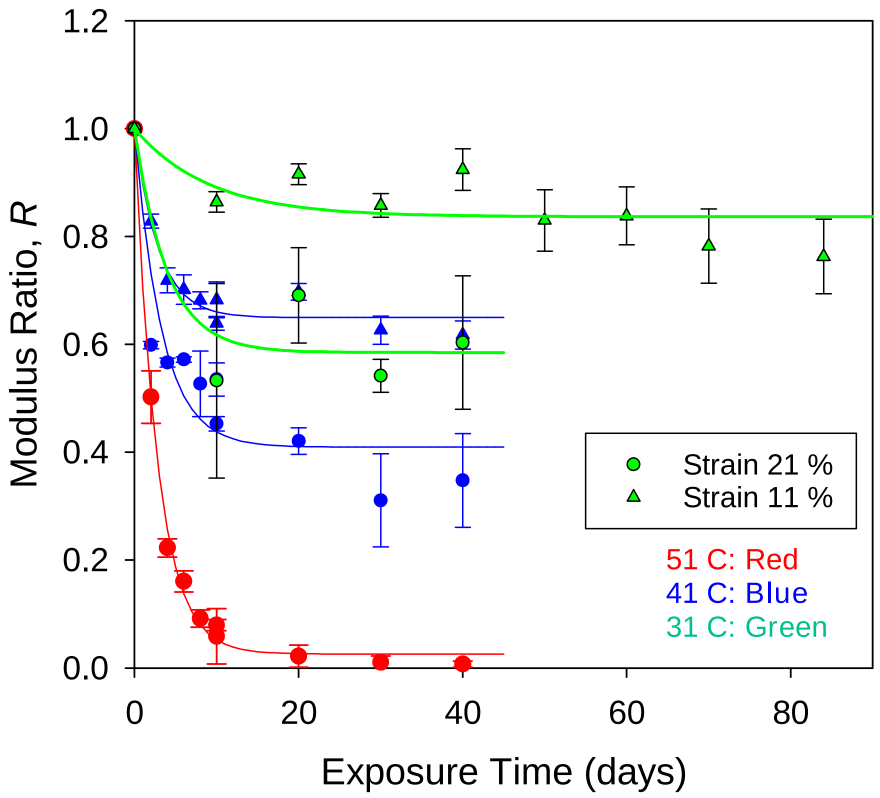
Kraton Behavior



- ❑ Does aging produce a simple downward shift in the stress relaxation curves for this material?
- ❑ Yes, although not always as simple as we would like.
- ❑ Calculate *R* at 100 s for various exposure times.

Trail with Kraton Data



- ❑ Not all 12 conditions show degradation in the times tested, but
- ❑ 5 most severe conditions do show significant changes.
  - – 21 % strain at 51 C,41 C, 31 C
  - – 11 % strain at 41 C, 31 C
  - – Each point is average of test on 4 specimens.
- ❑ Test 3 models
  - – Not zero order
  - – Not simple first order
  - – First order with limit provides a good fit of the data

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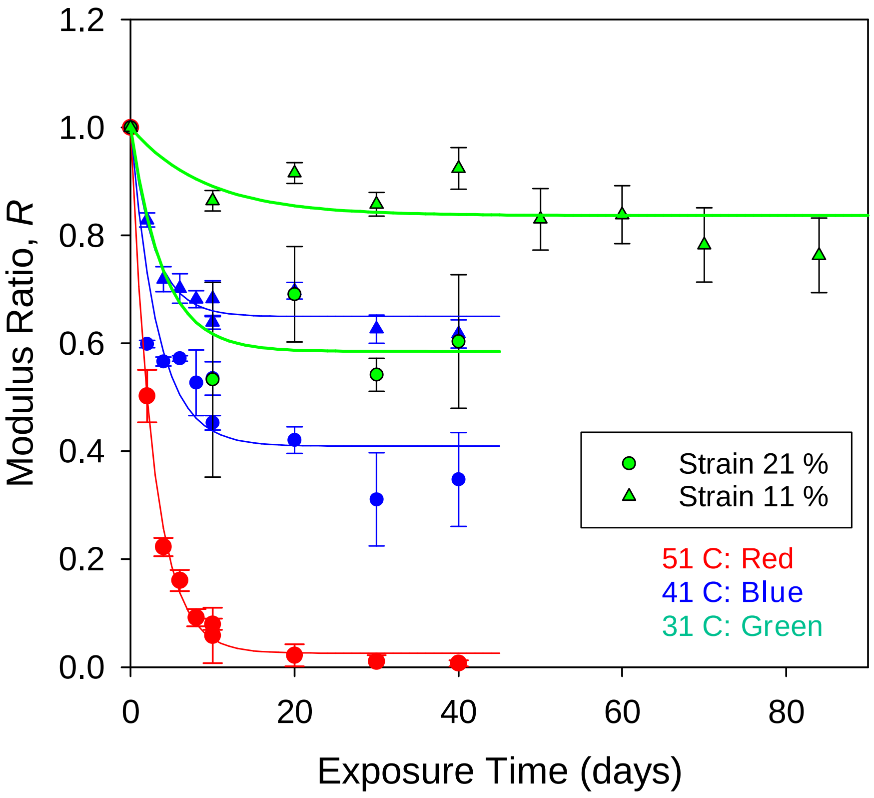
Test Model with Kraton

- ❑ Model is able to fit Kraton data at all 5 test conditions
- ❑ To test model, use data at right to determine parameters in equation
- ❑ Then conduct new tests and compare with predictions
- ❑ Use more complex exposure for test: two step experiment
  - ❖ **Expose sample at one set of environmental conditions**
  - ❖ **Then change to a second set of conditions and complete exposure**



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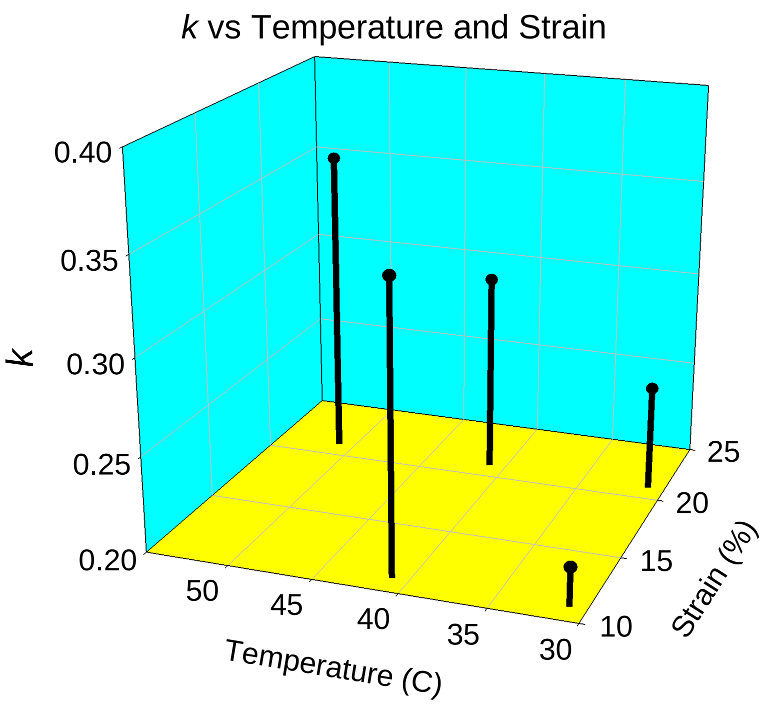
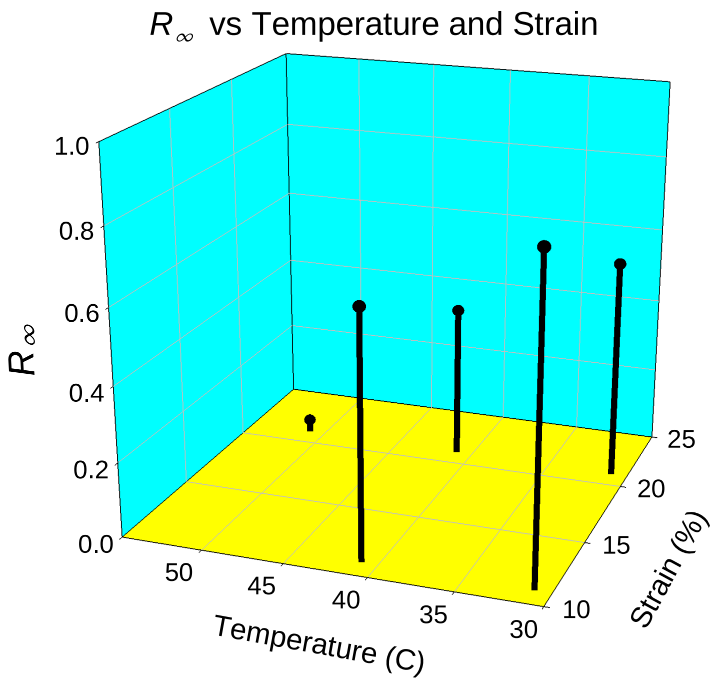
Determine Model Parameters



k vs Temperature and Strain

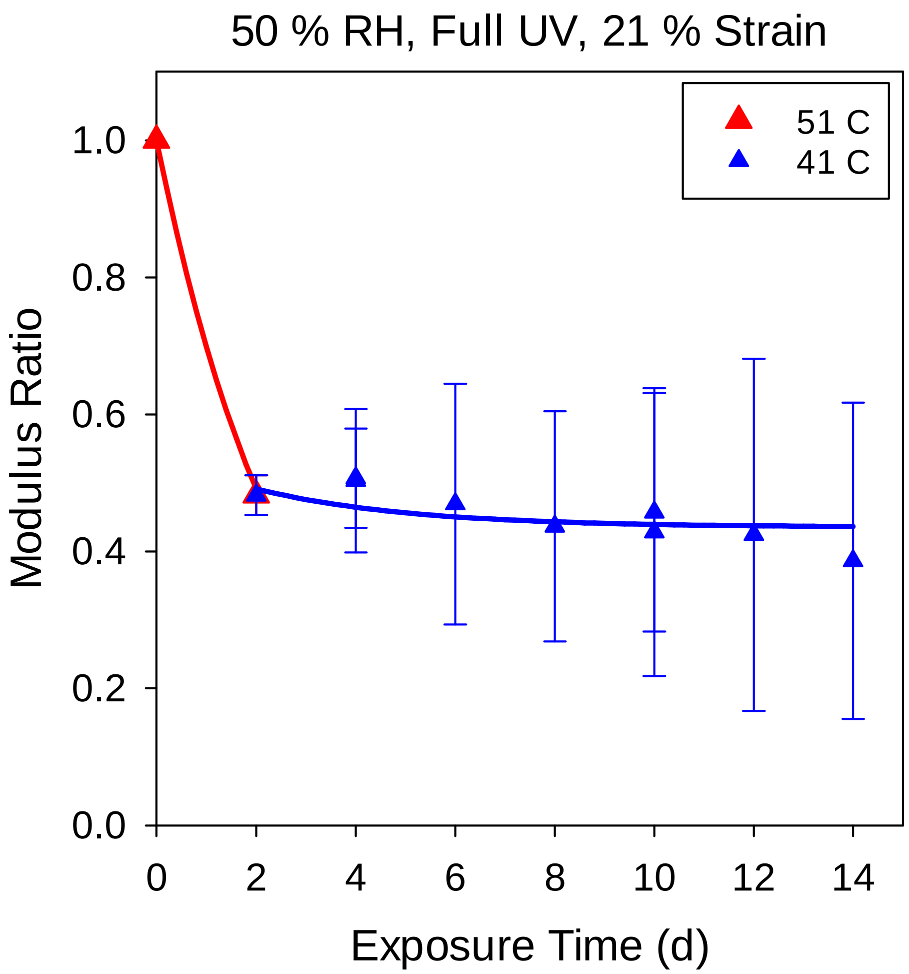


R_∞ vs Temperature and Strain

- ❑ Model parameters generally show the expected trends – more severe conditions have higher *k* and lower R_∞
- ❑ Can we use these parameters to predict behavior.

Use Data to Predict New Tests

- Good test of prediction capability is two step experiment – Three experiments
- Test 1: 50 % RH, Full UV, 21 % strain – 2 d at 51 C then 12 d at 41 C



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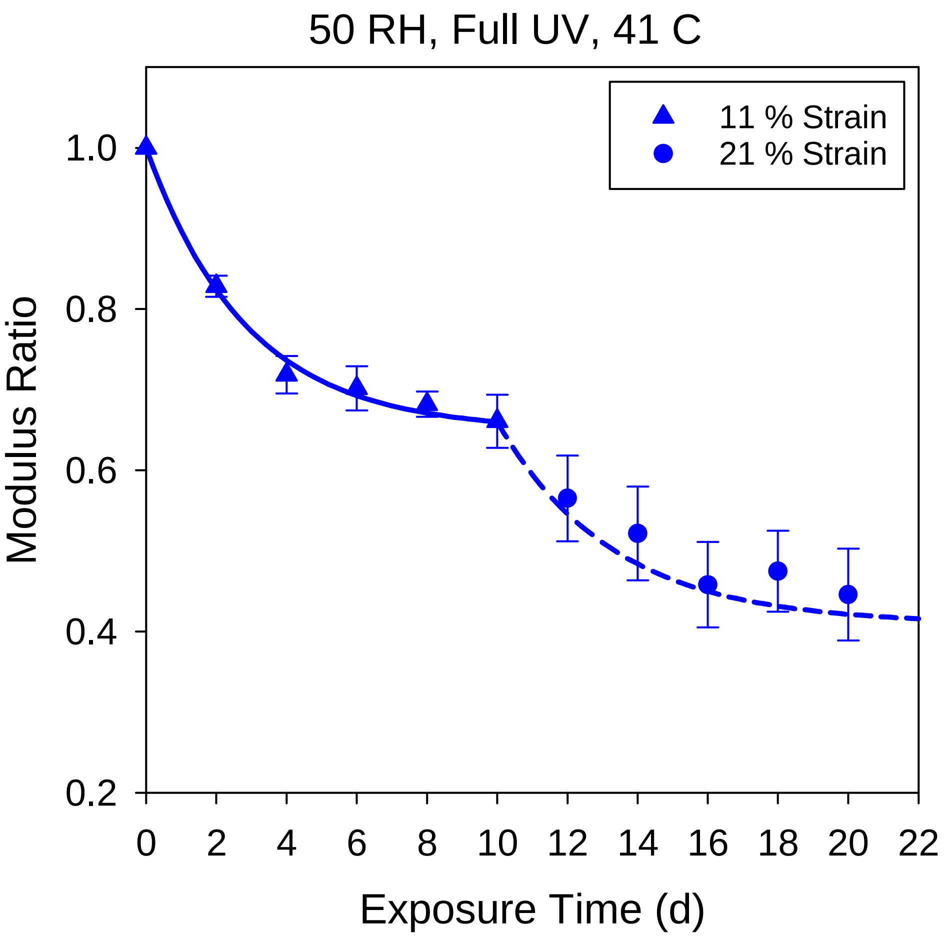
Use Data to Predict New Tests

- ❑ Good test of prediction capability is two step experiment – Three experiments.
- ❑ Test 1: 50 % RH, Full UV, 21 % strain – 2 d at 51 C then 12 d at 41 C.
- ❑ Test 2: 50 % RH, Full UV, 41 C – 10 d at 11 % strain then 10 d at 21 % strain.



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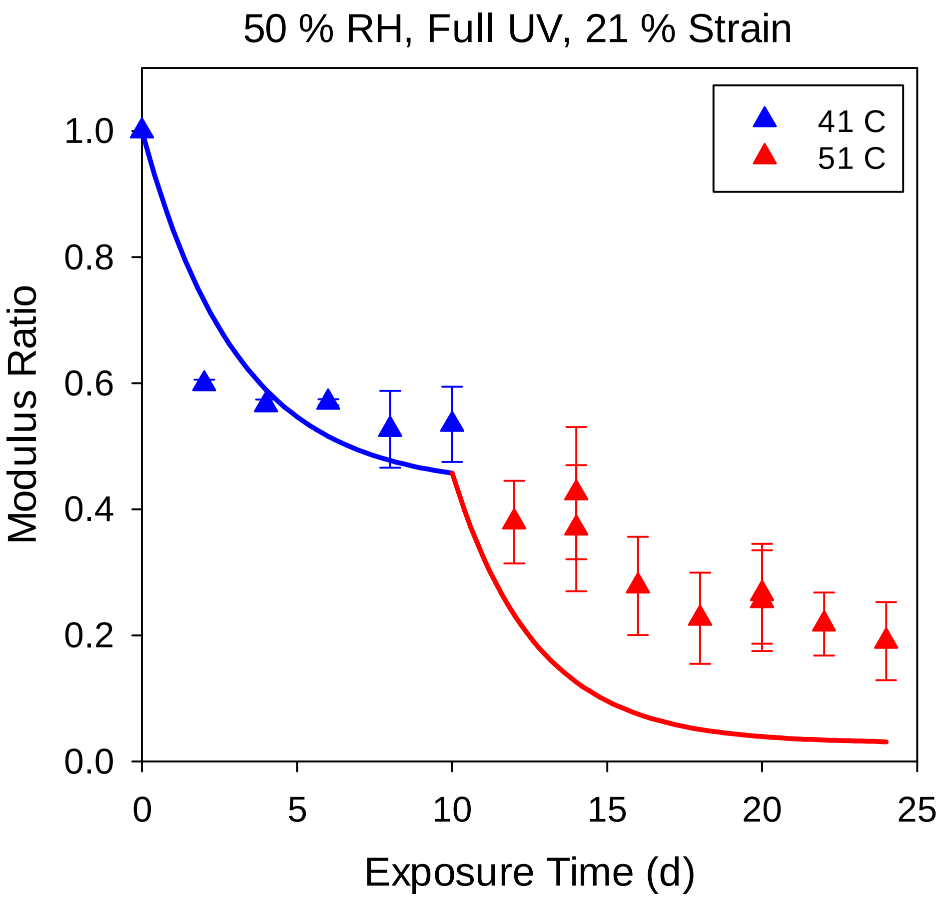
Use Data to Predict New Tests

- Good test of prediction capability is two step experiment – Three experiments.
- Test 1: 50 % RH, Full UV, 21 % strain – 2 d at 51 C then 12 d at 41 C.
- Test 2: 50 % RH, Full UV, 41 C – 10 d at 11 % strain then 10 d at 21 % strain.
- Test 3: 50 % RH, Full UV, 21 % strain – 2 d at 41 C then 12 d at 51 C
  - Captures trend but over predicts second step
  - Cracking may contribute to difference



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Conclusions

- Need additional data
  - More evaluation experiments
  - Additional sealants
  - Better understanding of how to include stain
  - Extend to include cracking
- Results are encouraging
  - Three different simple models to explore
  - All cases so far they capture trends in data
  - A number of cases have good agreement
  - Have know assumptions