Polymers/Organic Materials Aging Overview

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National Nuclear Security Administration

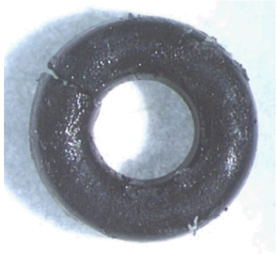
Mutual Interests

Problems of National Interest
-High Reliability
-High Consequence
-Long Term Concerns

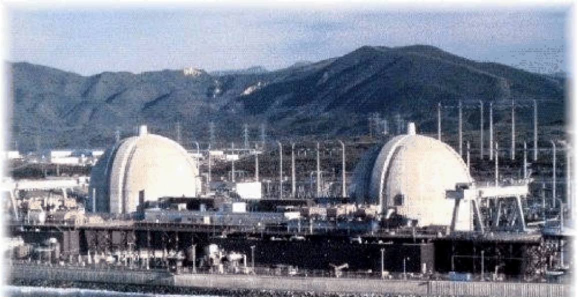
Goal of visit/talk:

1) Explain how we approach organic material aging
2) Learn how you do organic material aging
3) Look for learning opportunities/collaborations
4) Act as messenger/middle men for other areas of similar concern (solder, corrosion, ceramics etc etc)
5) Open lines of communication similar to what we have with our UK counterparts

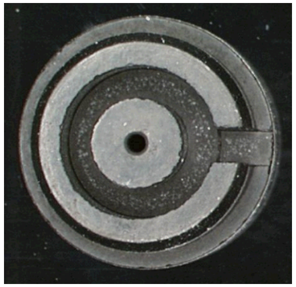
Organic Materials Problems;
Organic Materials Aging and Degradation



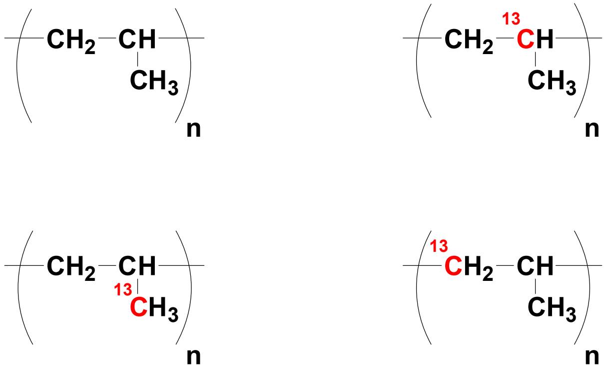
O-rings



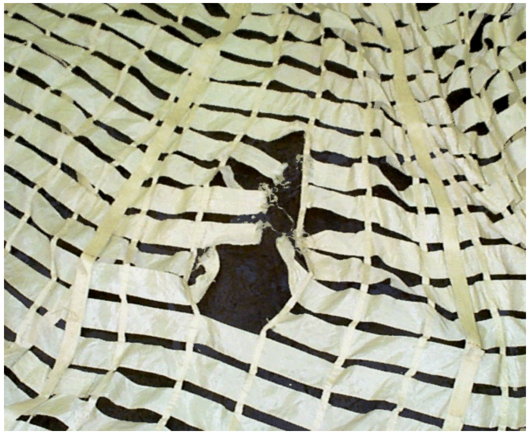
Nuclear Power Plant Cable Insulation



Shorting Plugs

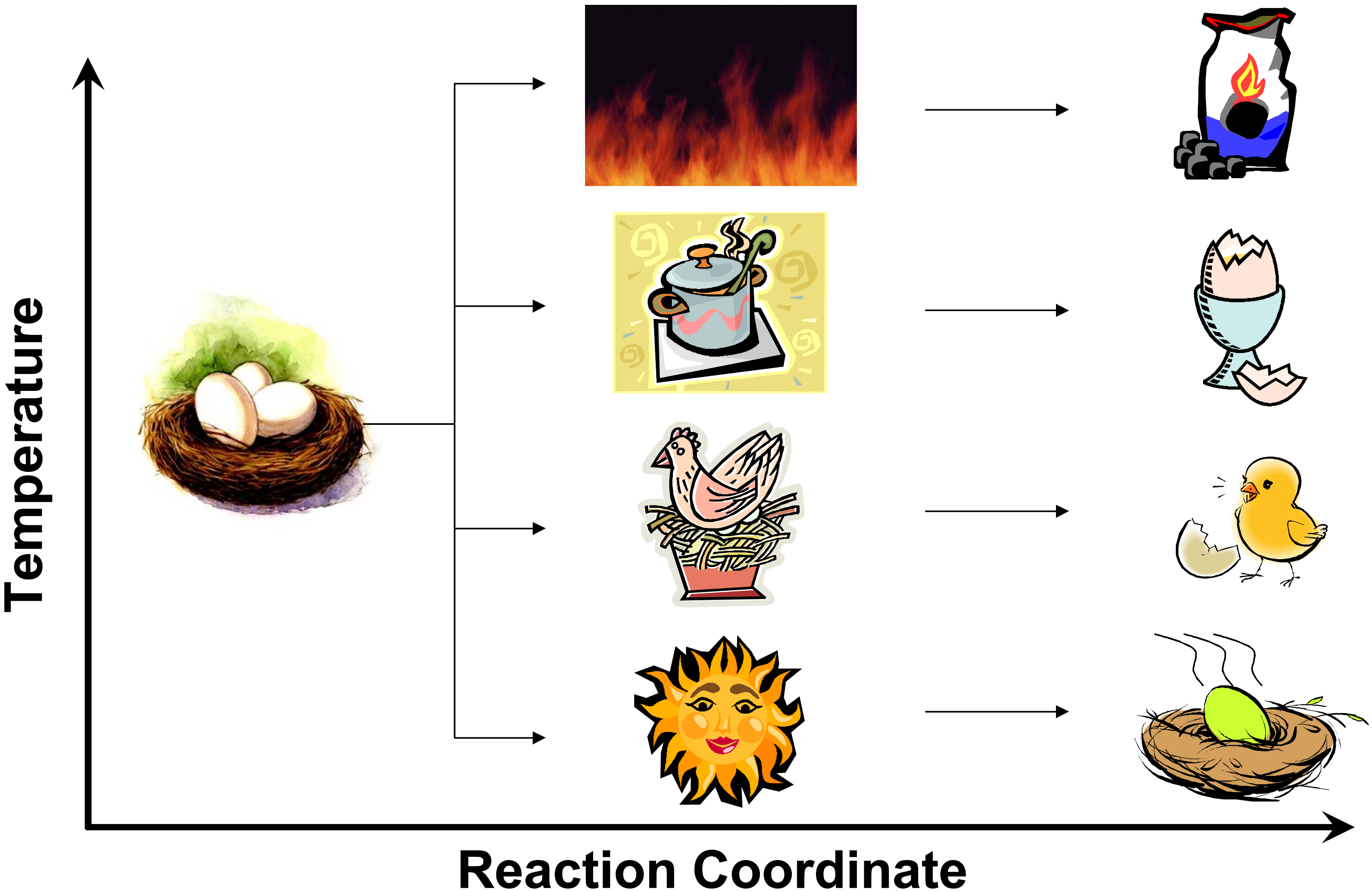


Labeled Polymers



Textiles

‘Accelerated Aging’



General Approach/Goals

Macroscopic level

Physical property

Sealing Force

Compression Set

Tensile Strength

Permeation

Elongation

Dimensional changes

Molecular Level

Chemical Property

UV-VIS Spectroscopy

Surface Analysis

Differential Scanning Calorimetry

Additives

Molecular Weight Analysis

Infra-red Spectroscopy

X-Ray Analysis

Density

Nuclear Magnetic Resonance

GPC

Goals

- Prediction of physical properties vs. time
    - Predict remaining ***lifetime*** of field materials
- Develop condition monitoring method

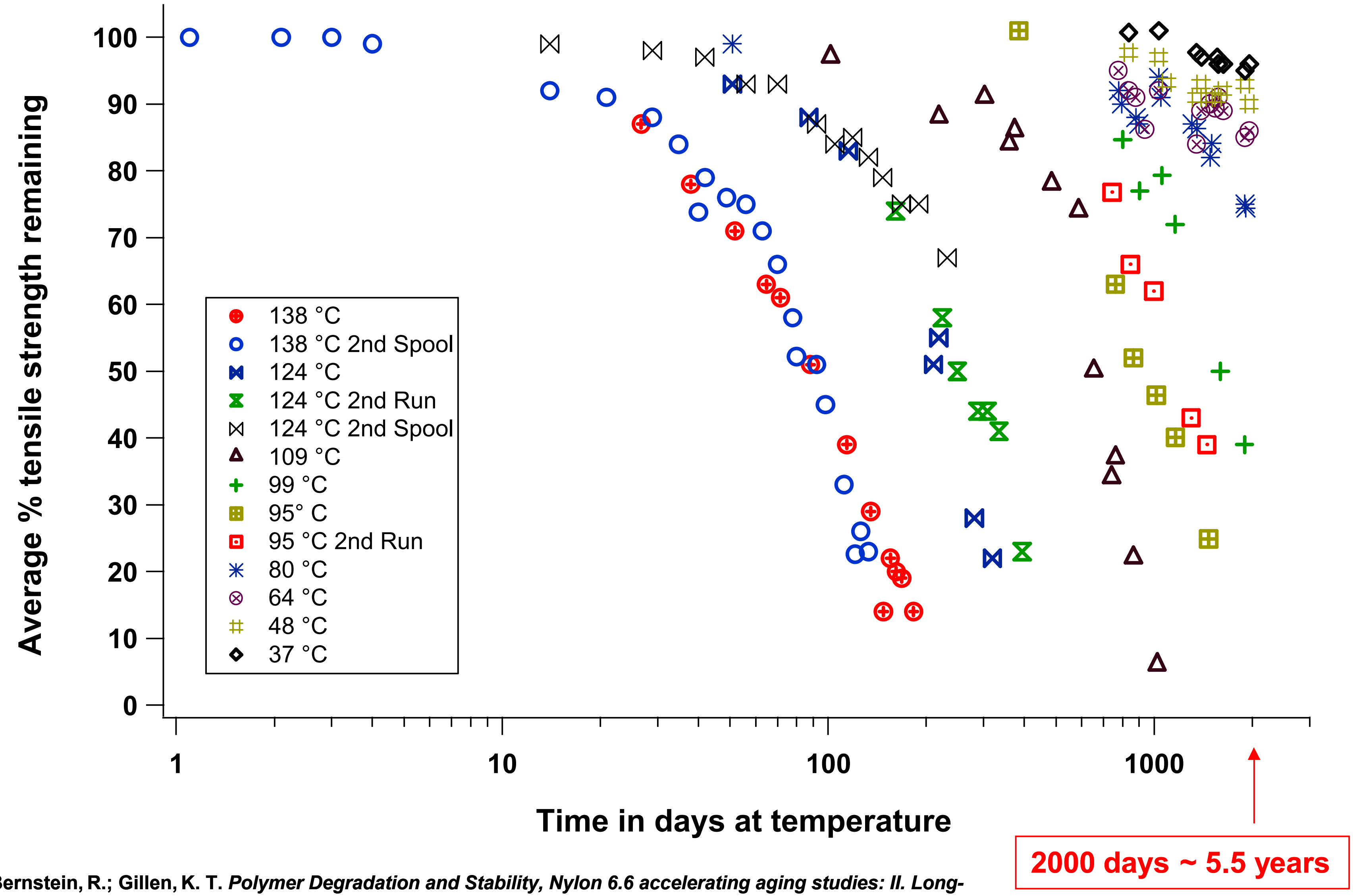
Deception!

Conclusions derived from initial high temperature, short duration (even out to 1 year) accelerated aging can be misleading.

Chemistry / mechanisms must be understood.

Results must be critically analyzed to identify and understand mechanism changes

Thermal-oxidative Aging: Nylon



Bernstein, R.; Gillen, K. T. *Polymer Degradation and Stability, Nylon 6.6 accelerating aging studies: II. Long-term thermal-oxidative and hydrolysis results 2010, 95, 1471-1479.*

Arrhenius Equation

Arrhenius equation:

$$k = Ae^{-Ea/RT}$$

Old Chemist expression:
increase rate by 10 °C will double the rate

Time Warp

Back to High School….

…..but only briefly….

Equation of a Line

$$y=mx + b$$

y-intercept

what you want

what you know

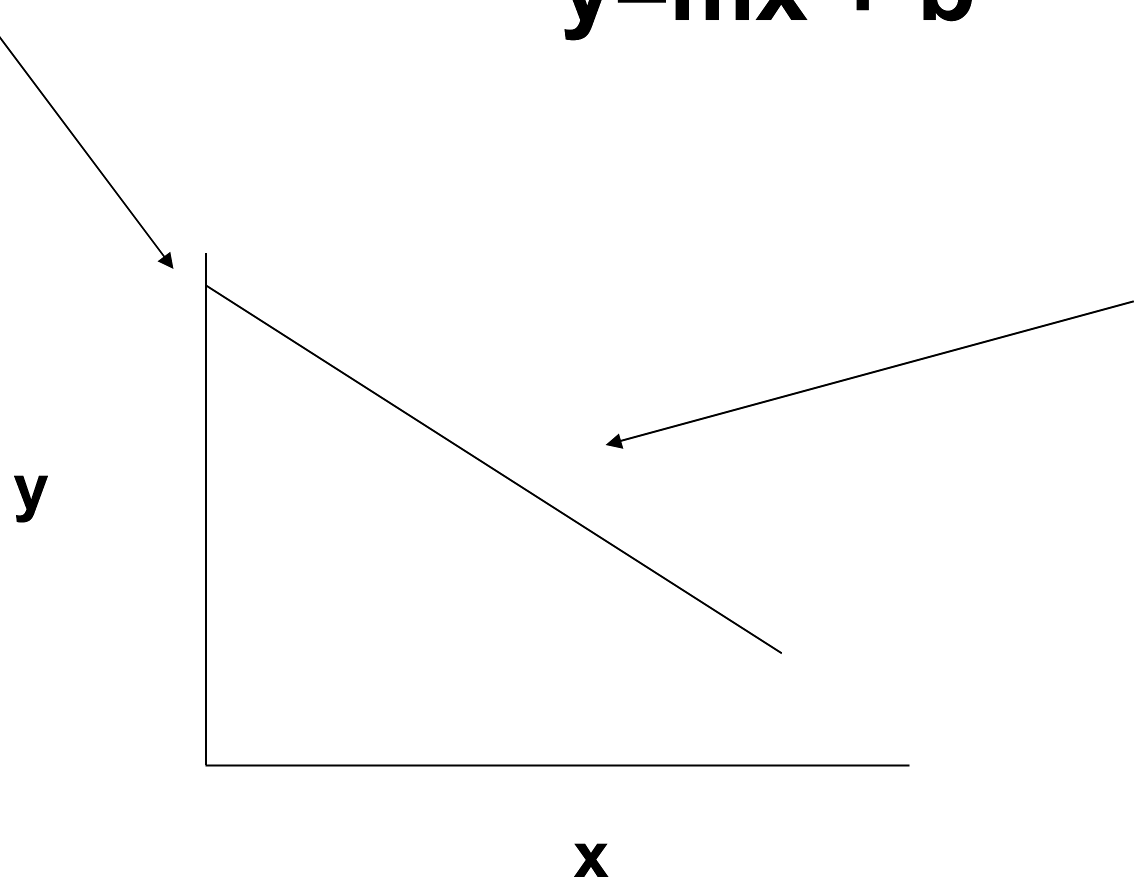
slope

Function of a Line

y intercept =b

$$y=mx + b$$

slope =m



Arrhenius Equation

Activation Energy

$$k = Ae^{-E_a/RT}$$

rate

Gas constant

Temperature (Kelvin)

Pre-exponential factor

e

Empirical equation

Arrhenius Equation

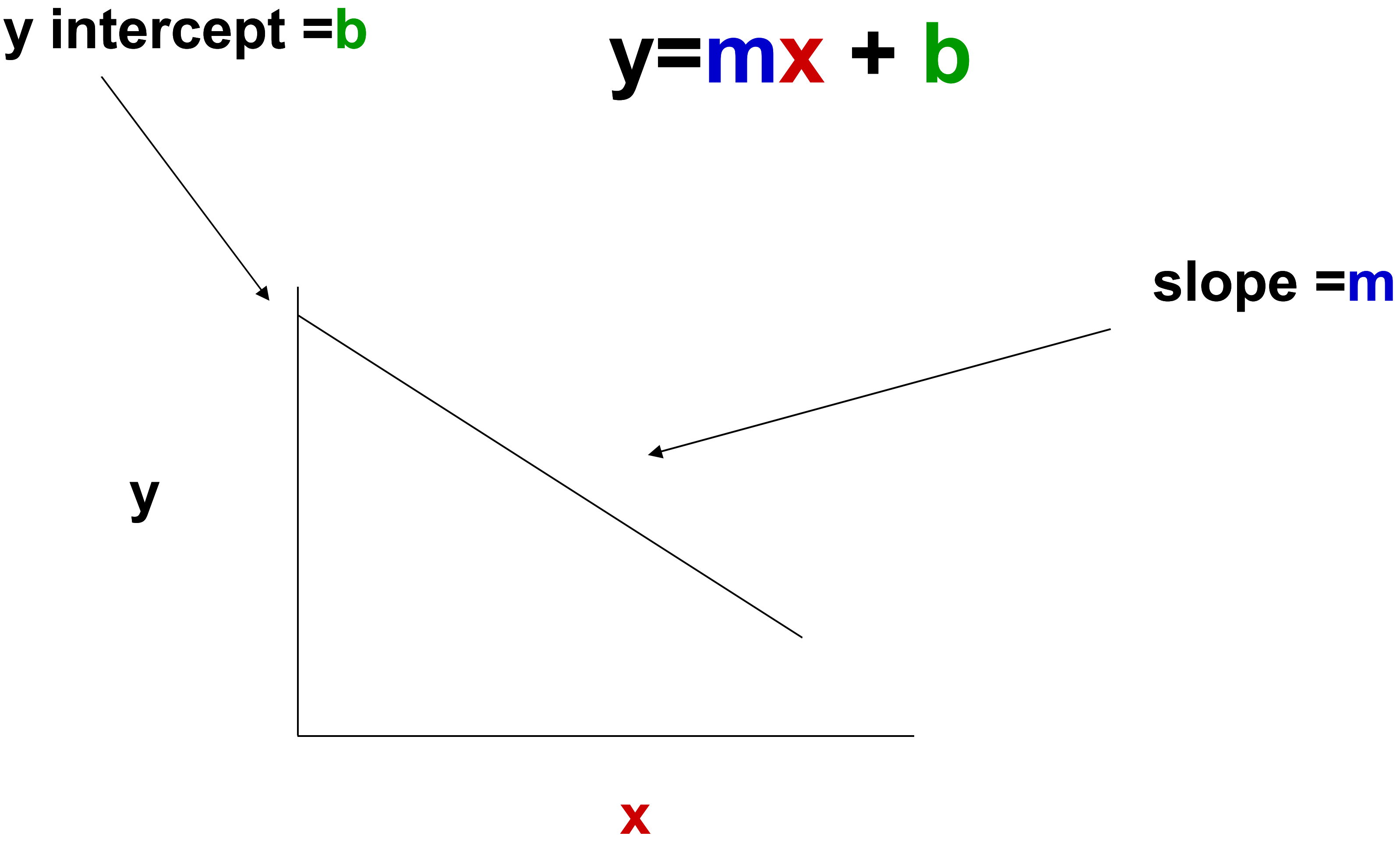
$$k = Ae^{-Ea/RT} \longrightarrow \ln(k) = \ln(A) - Ea/RT$$

$$\ln(k) = -Ea/RT + \ln(A)$$

$$\ln(k) = -(Ea/R)(1/T) + \ln(A)$$

Function of a Line

$$y = mx + b$$

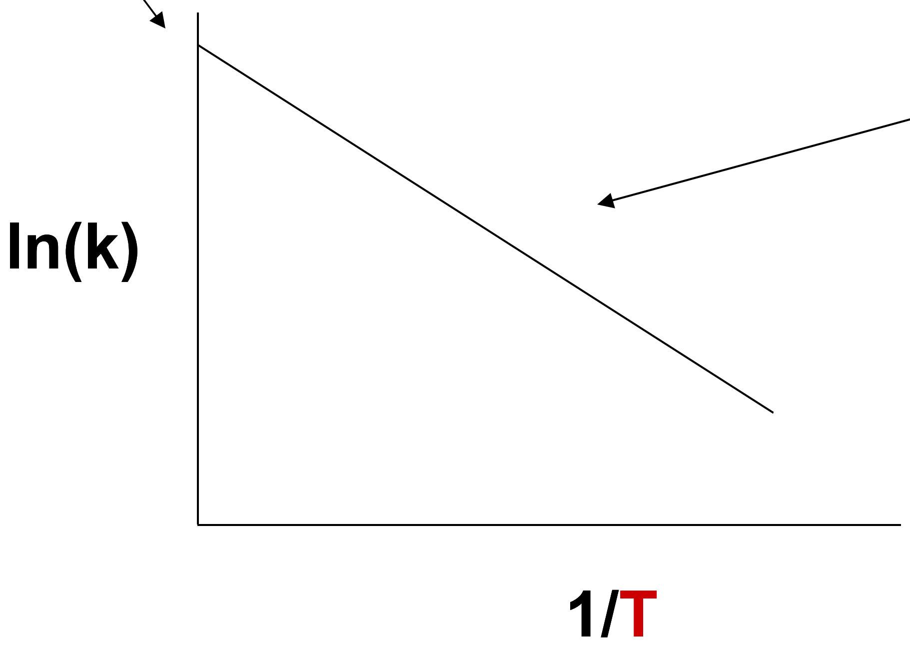


Function of a Line

y intercept = ln(A)

$$\ln(k) = -(E_a/R)(1/T) + \ln(A)$$

slope = -Ea/R



Arrhenius Equation

Arrhenius equation:

$$k = Ae^{-Ea/RT}$$

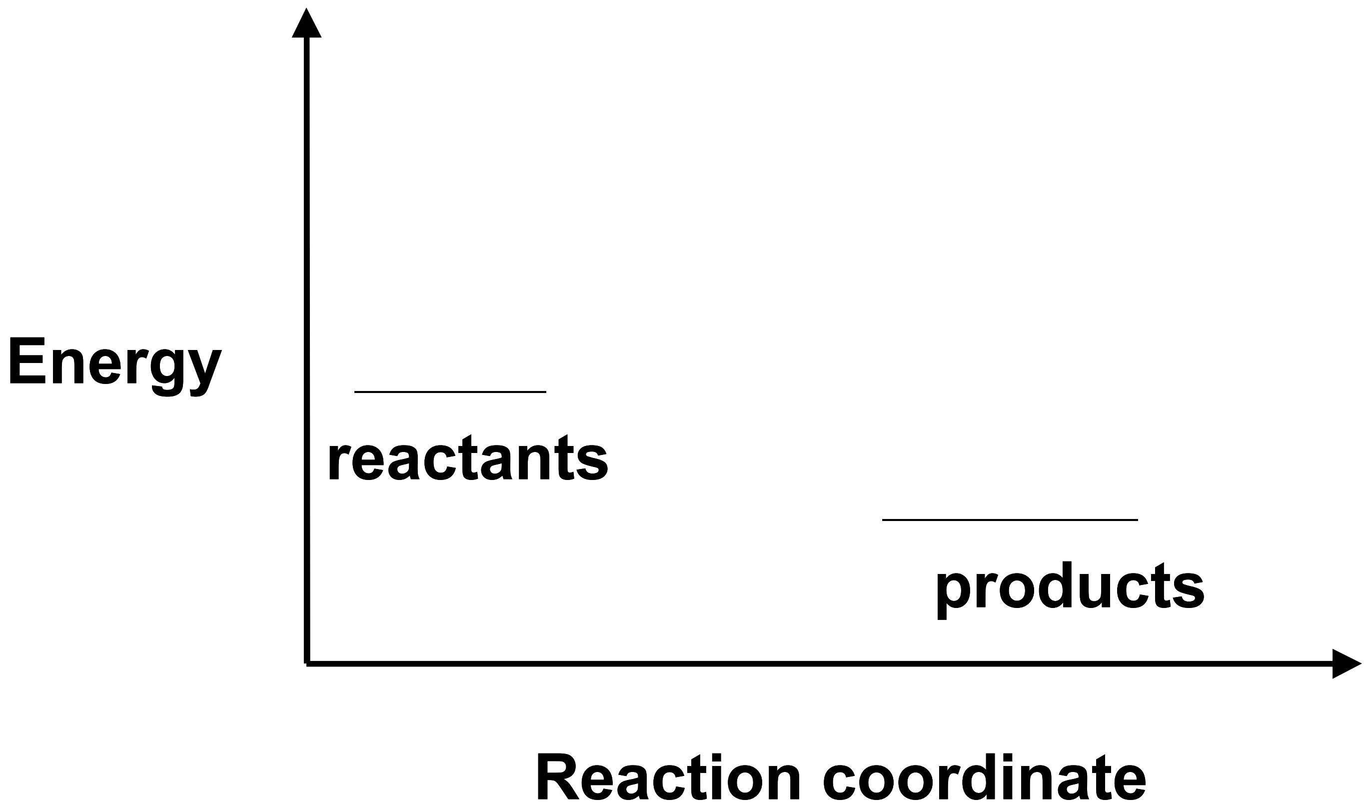
$$\ln(k) = -(Ea/R)(1/T) + \ln(A)$$

k = anything

Plot $\log(a_T)$ vs 1/T linear if Arrhenius

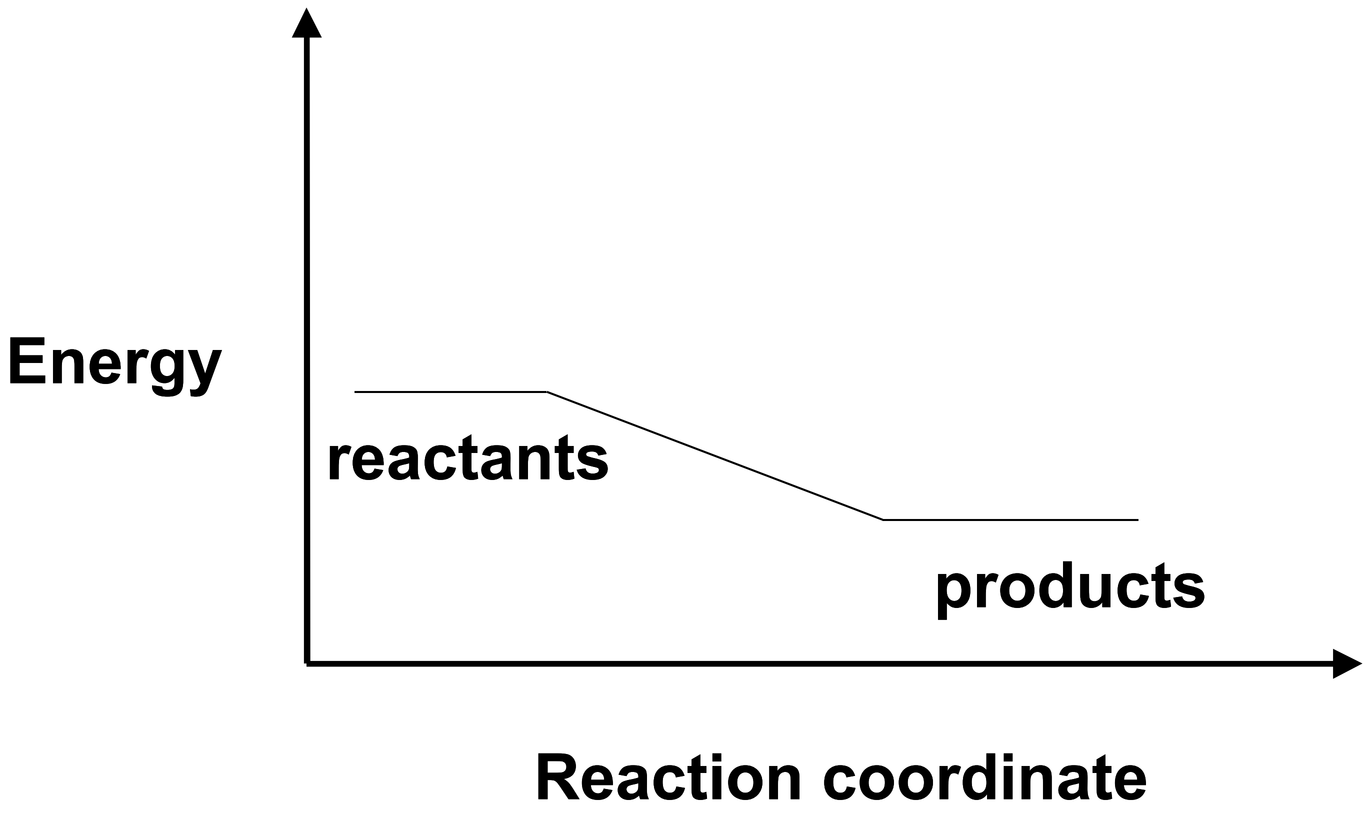
What is Ea?

E_a

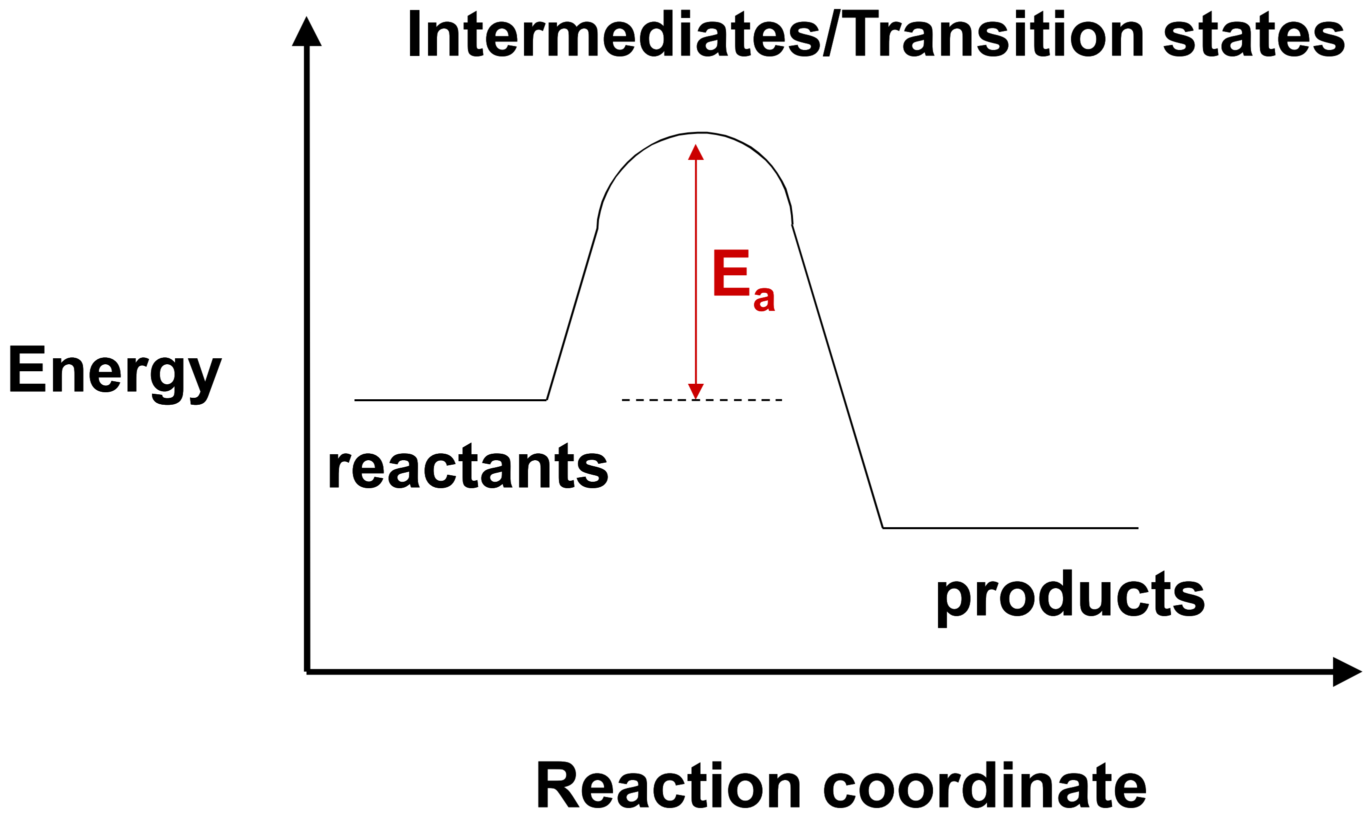


---Imagine a marble---

E_a

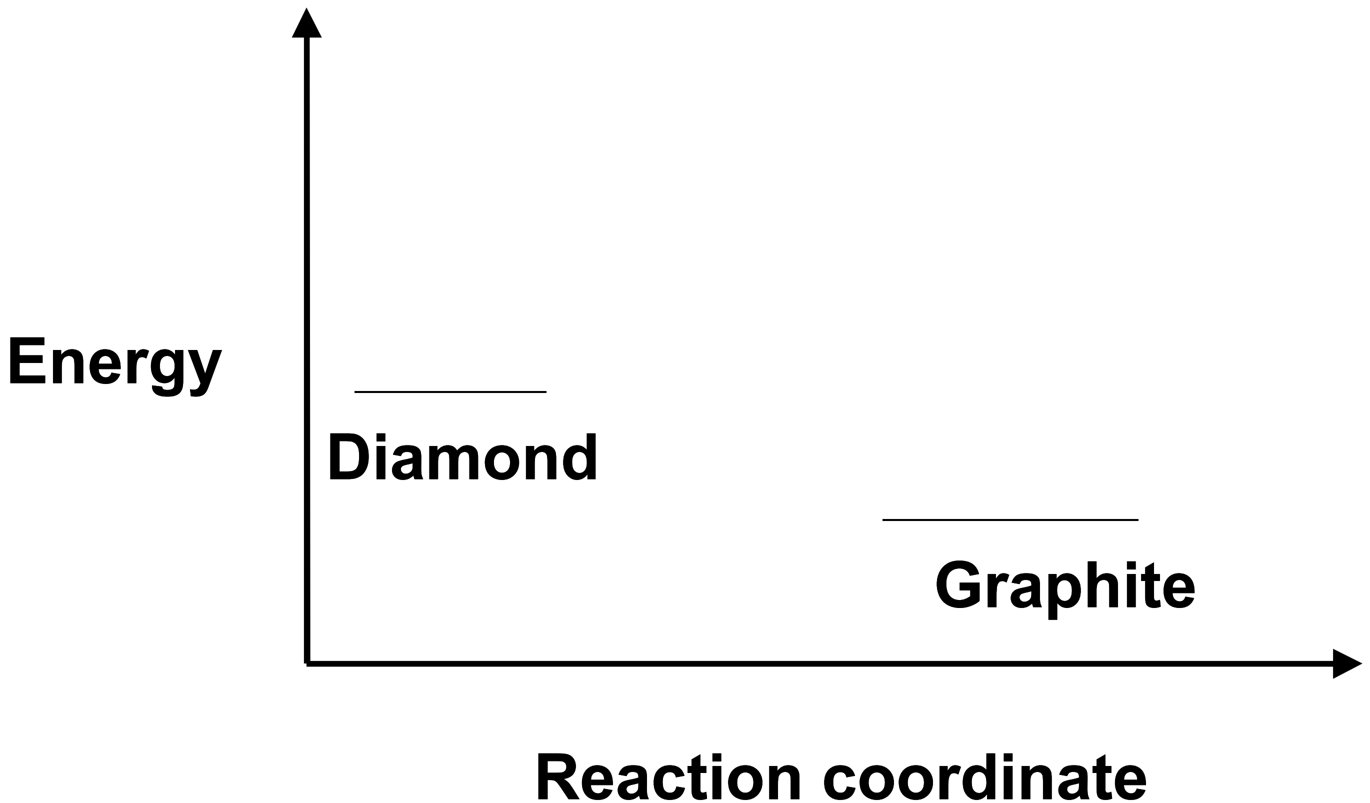


E_a

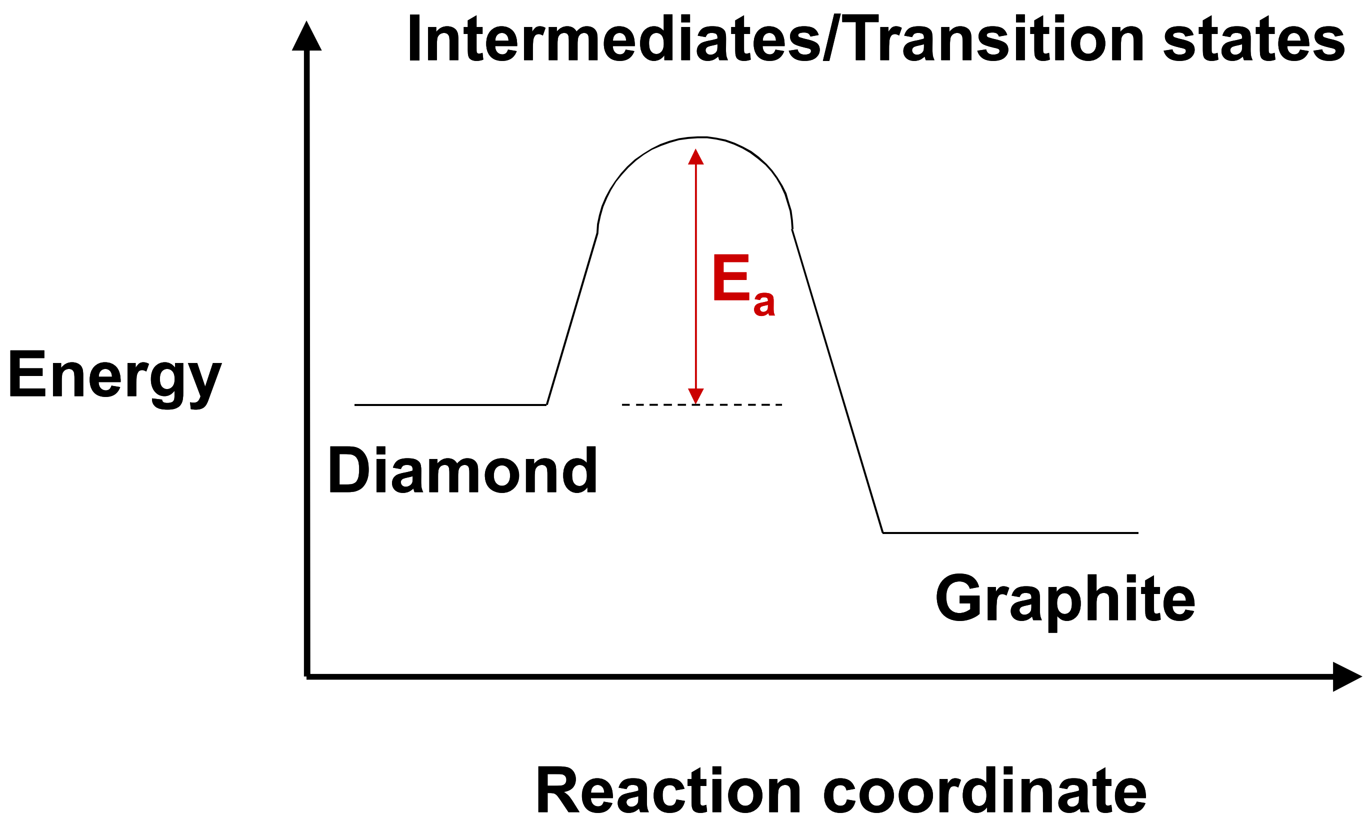

Intermediates/Transition states
Energy
Ea
reactants
products
Reaction coordinate

Are Diamonds *forever*?

Kinetics vs. Thermodynamics (really the same thing)



E_a



Intermediates/Transition states
Energy
E
a
Diamond
Graphite
Reaction coordinate

Arrhenius Equation

$$k = Ae^{-Ea/RT}$$

Critical assumption is that E_a is CONSTANT

Assume

Ass-u-me

Time-Temperature Superposition

Does mechanism change as a function of temperature?

If same mechanism:

- same shape (log graph)
- should be constant acceleration (multiple)

1. Pick a reference temperature
2. Multiply the time at each temperature by the constant that gives the best overlap with the reference temperature data
3. Define that multiple as 'a_T' (a_T = 1 for ref. temp.)
4. Find a_T for each temperature

Plot $\log(a_T)$ vs 1/T linear if Arrhenius

Gillen, K. T.; Celina, M.; Clough, R. L.; Wise, J. *Trends in Polymer Science,* Extrapolation of Accelerated Aging Data -Arrhenius or Erroneous? **1997**, *5*, 250-257.

Arrhenius equation: Empirical equation

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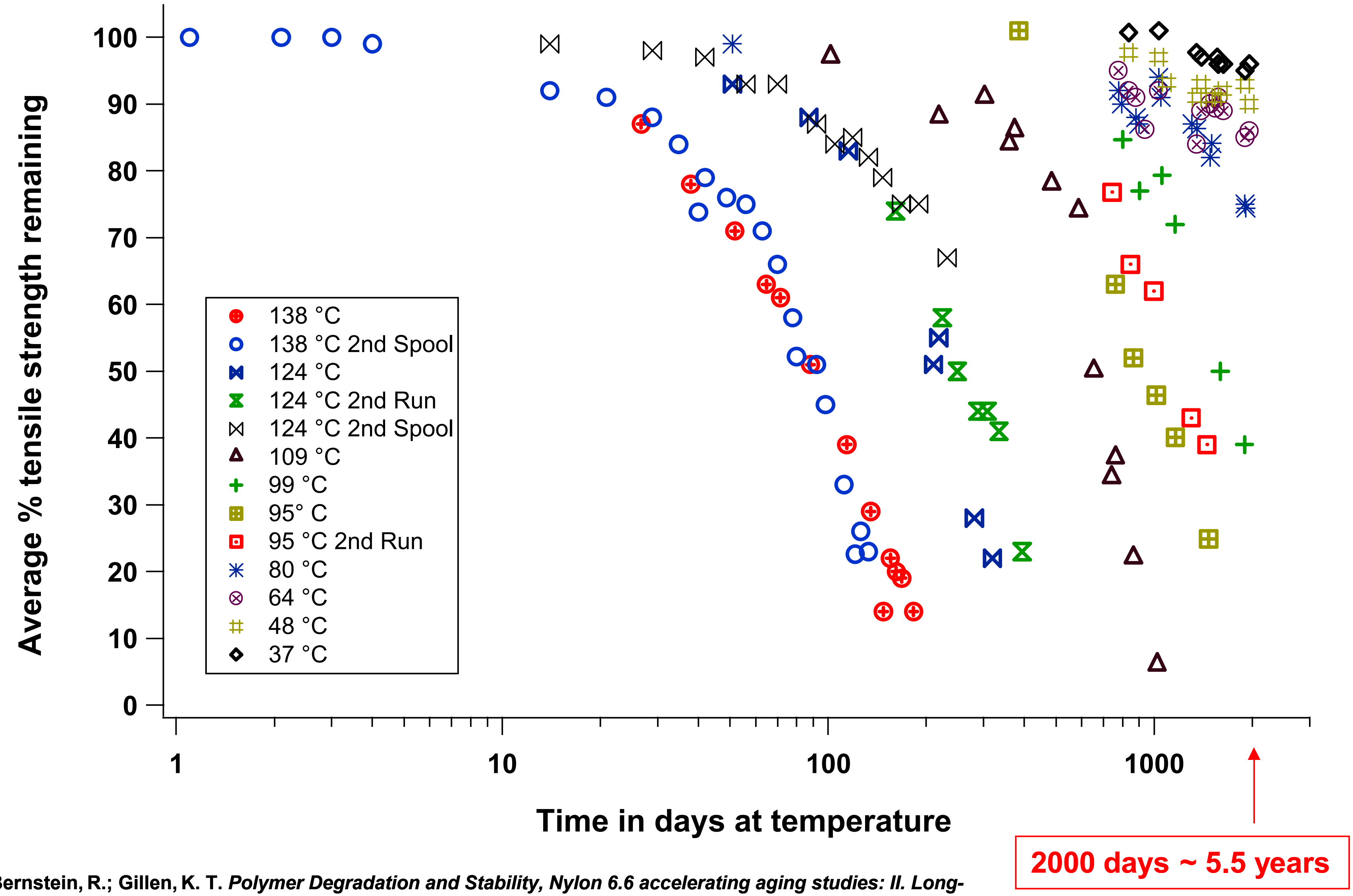
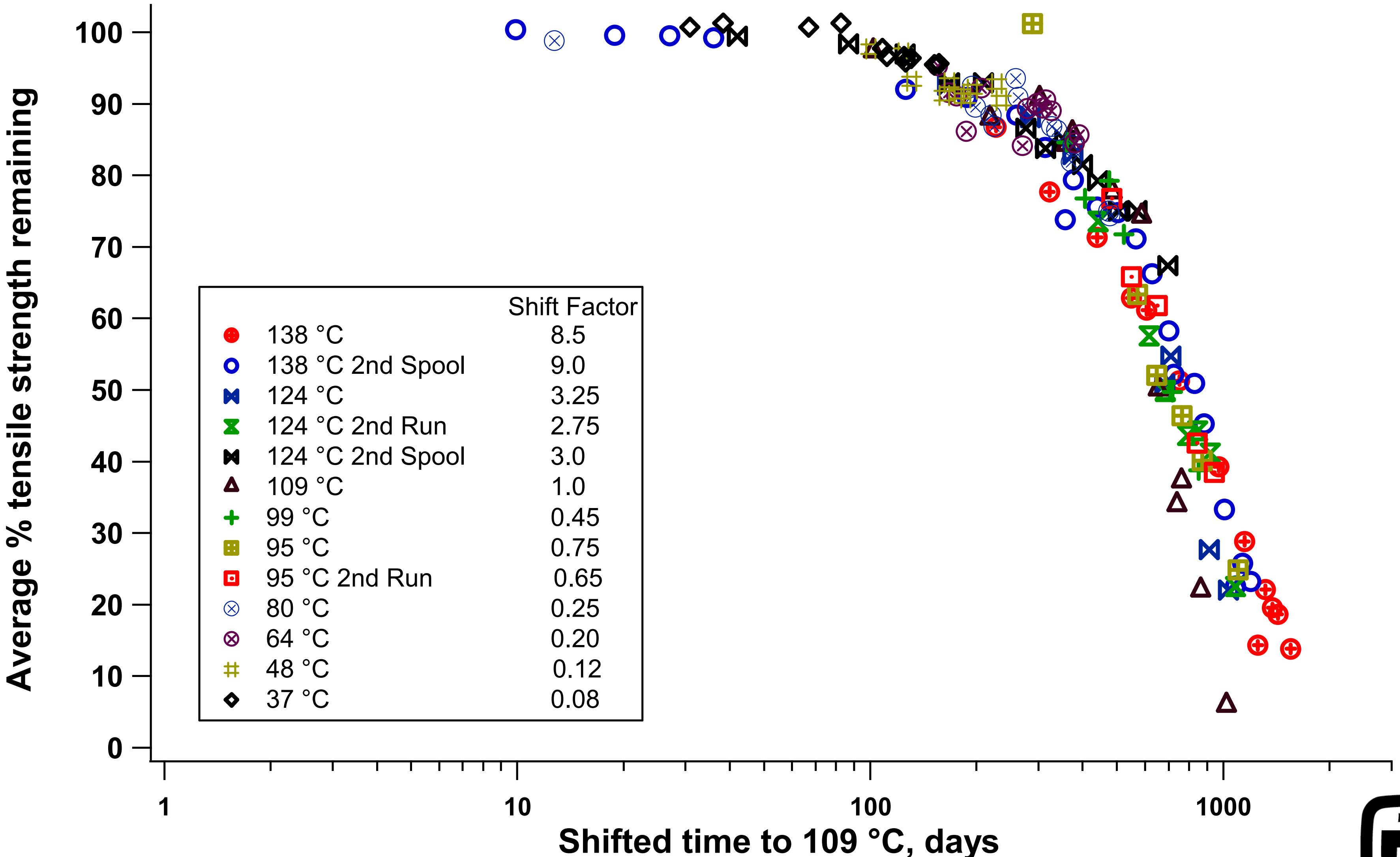
$$\ln(k) = \ln(A) - Ea/RT$$

Thermal-oxidative Aging: Nylon



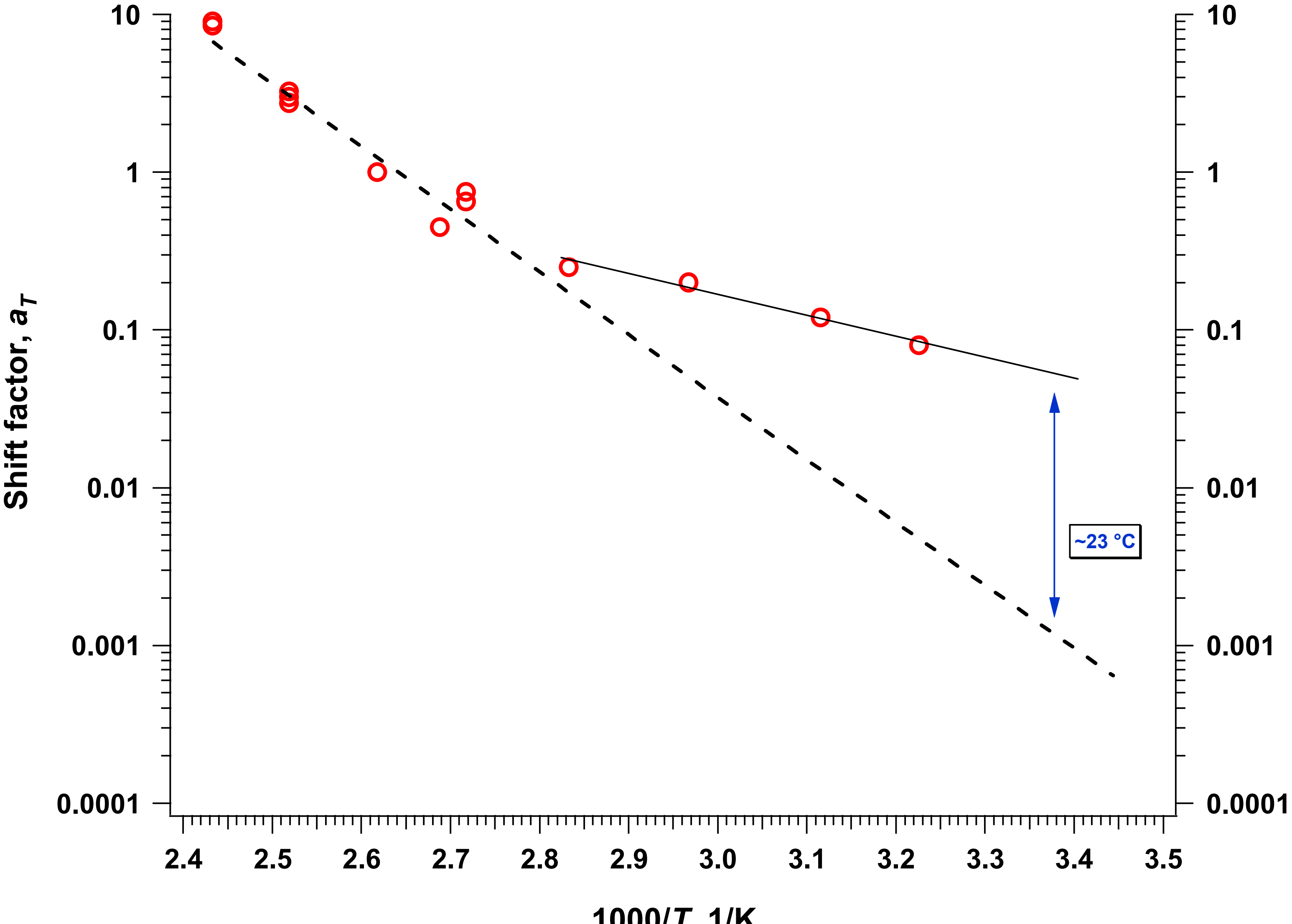
Bernstein, R.; Gillen, K. T. *Polymer Degradation and Stability, Nylon 6.6 accelerating aging studies: II. Long-term thermal-oxidative and hydrolysis results 2010, 95, 1471-1479.*

Thermal-oxidative Aging: Nylon Shifted Data



Bernstein, R.; Gillen, K. T. *Polymer Degradation and Stability, Nylon 6.6 accelerating aging studies: II. Long-term thermal-oxidative and hydrolysis results 2010, 95, 1471-1479.*

Thermal-oxidative Aging: Nylon Shift Factor Graph



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Thermal Exposure

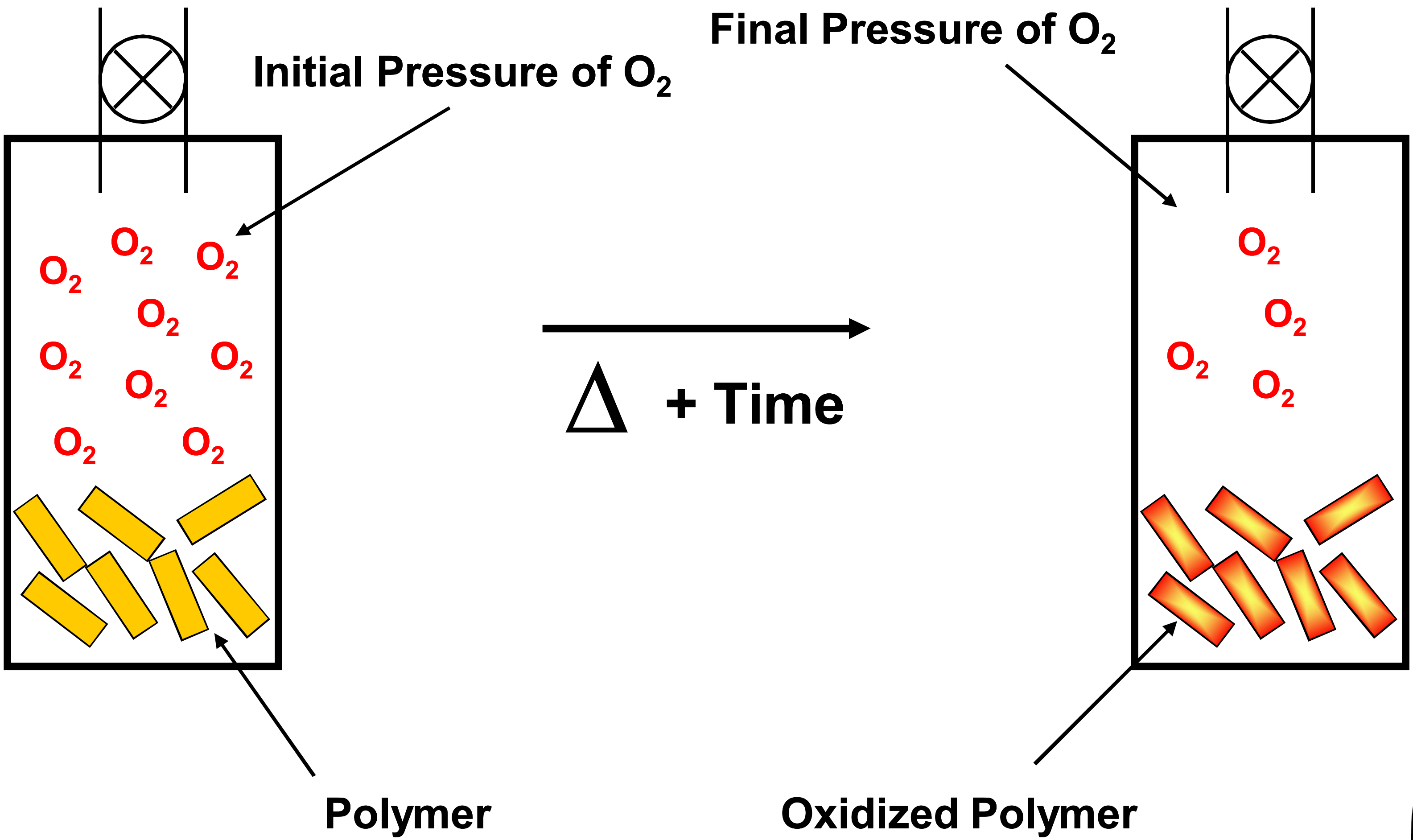
Thermal-Oxidation

$$\text{Polymer} + O_2 \longrightarrow \text{Oxidized Polymer}$$

Quantify amount of oxygen consumed

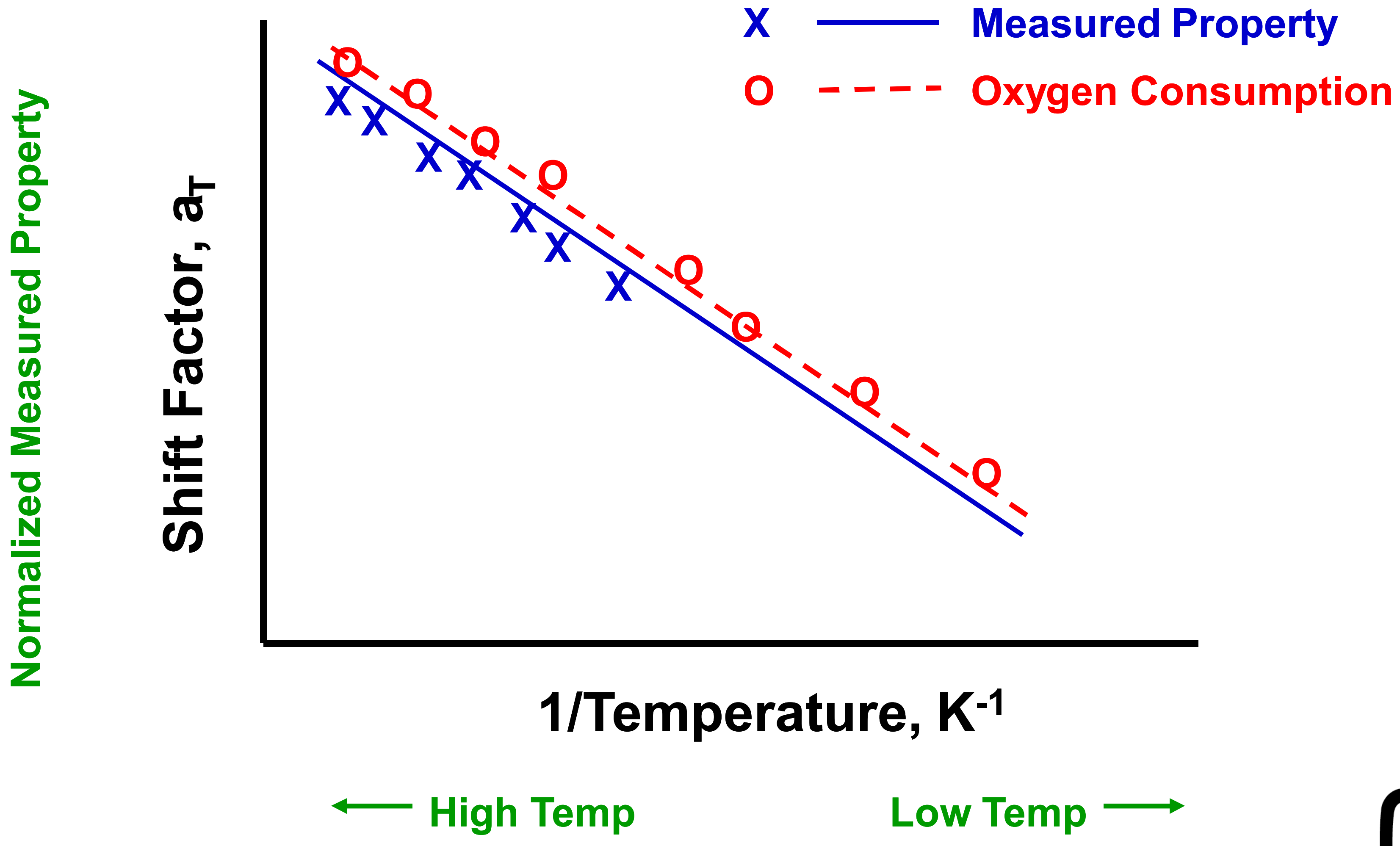
- Simple in theory
- Difficult in practice
- Amazingly sensitive

Schematic of Oxuptake

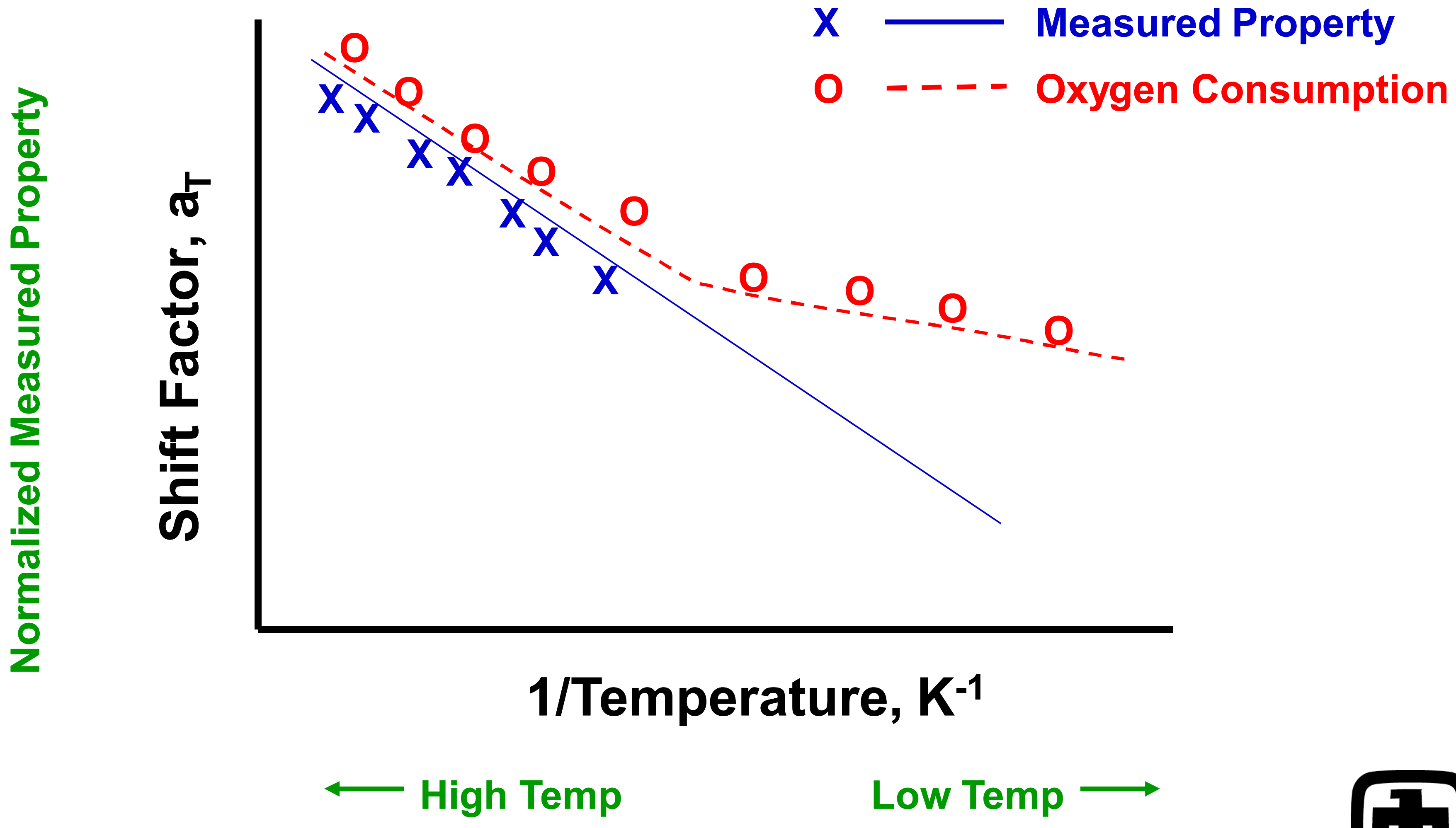


Oxygen Consumption

Enhanced Extrapolation 'Good'



Enhanced Extrapolation: 'Bad'



DLO, Need to Know

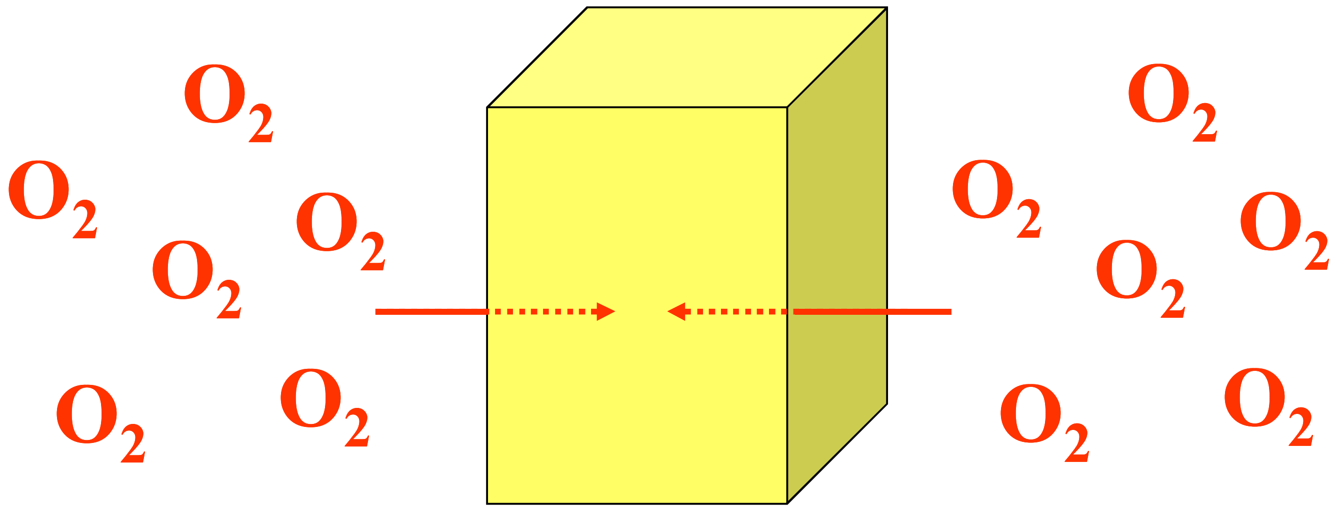
Diffusion Limited Oxidation (DLO) effects if oxygen dissolved in material used up faster by reaction than it can be replenished by diffusion from surrounding air atmosphere

Race between:
the oxygen consumption rate versus the oxygen diffusion rate

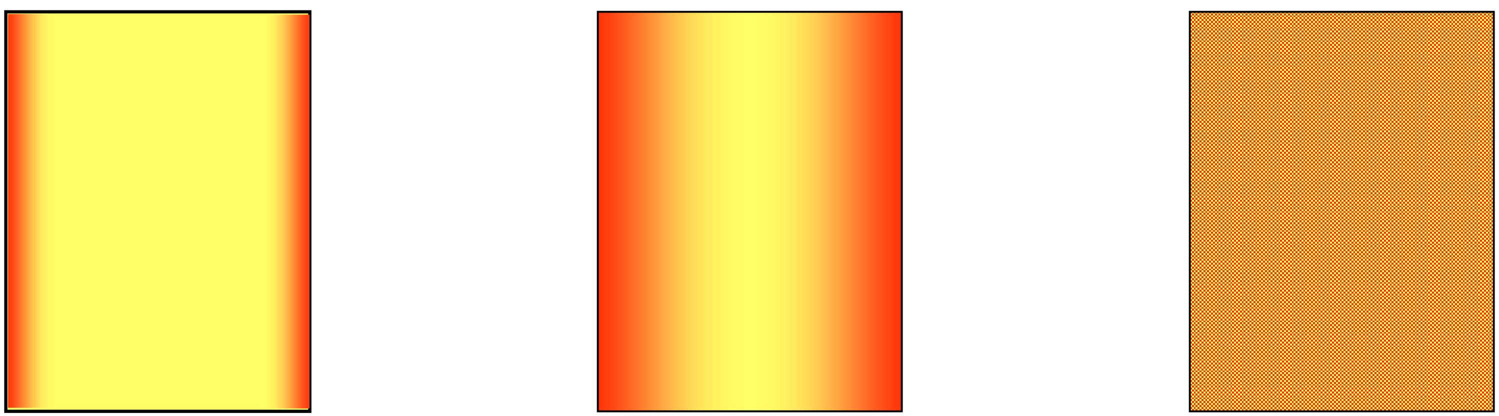
Therefore we need estimates of:

1. O_2 permeability versus aging temperature
2. O_2 consumption versus aging temperature

Diffusion-Limited Oxidation (DLO)



rxn rate > diffusion rate **rxn rate < diffusion rate**



Heterogeneous **Homogeneous**

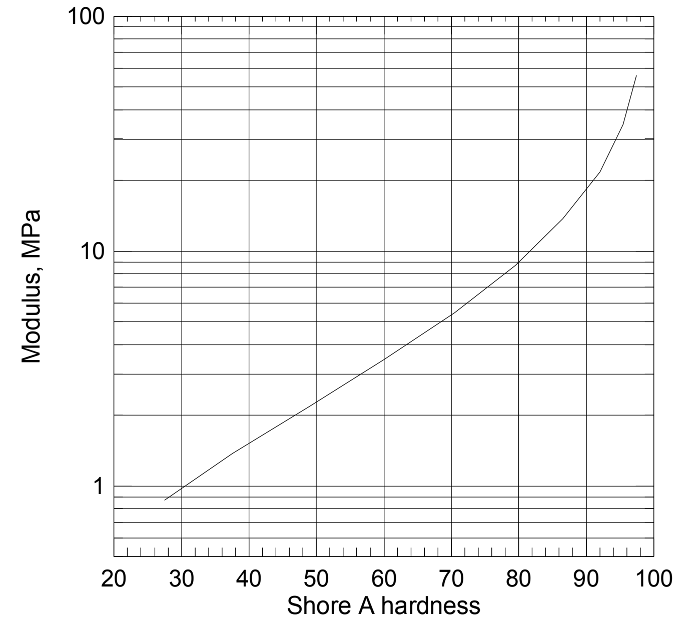
Modulus Profiling

Indentation technique
ca. 50μm resolution

Measure of Inverse tensile compliance

Closely related to tensile modulus

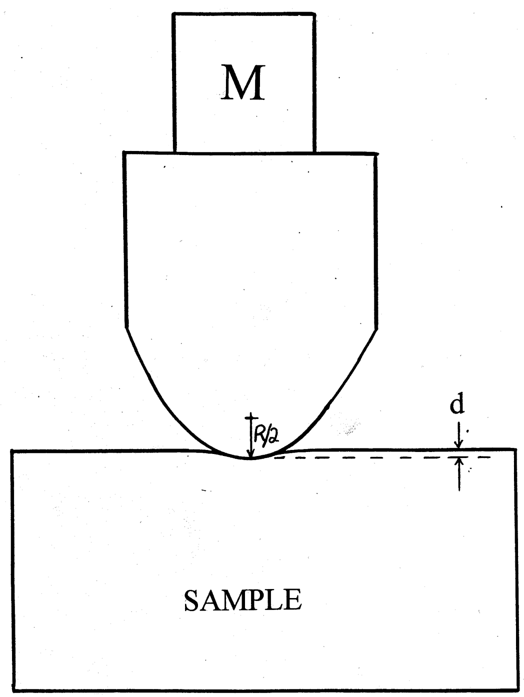
Modulus vs. Shore A



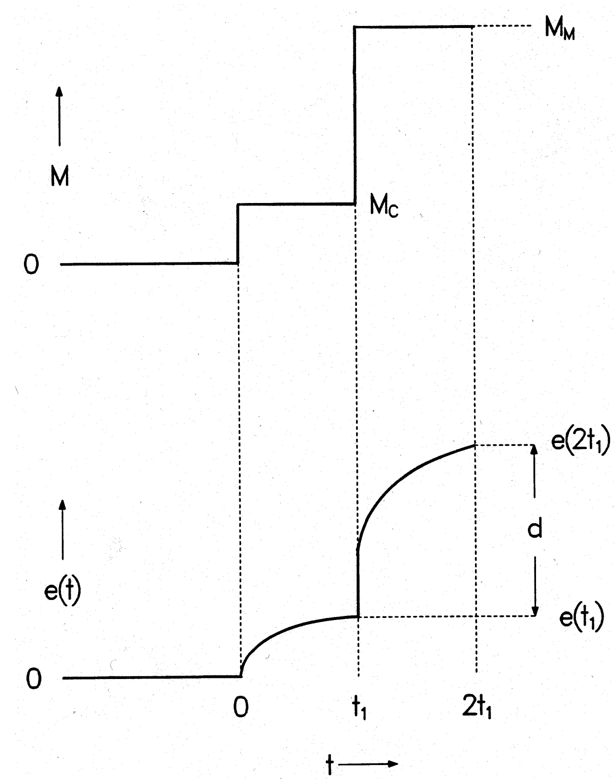
Excellent to examine 'geneity' of aging (heteo- or homo-) (DLO issues)

Schematic of Modulus Profile Experiment

Probe tip, sample and mass



Mass is applied in two steps



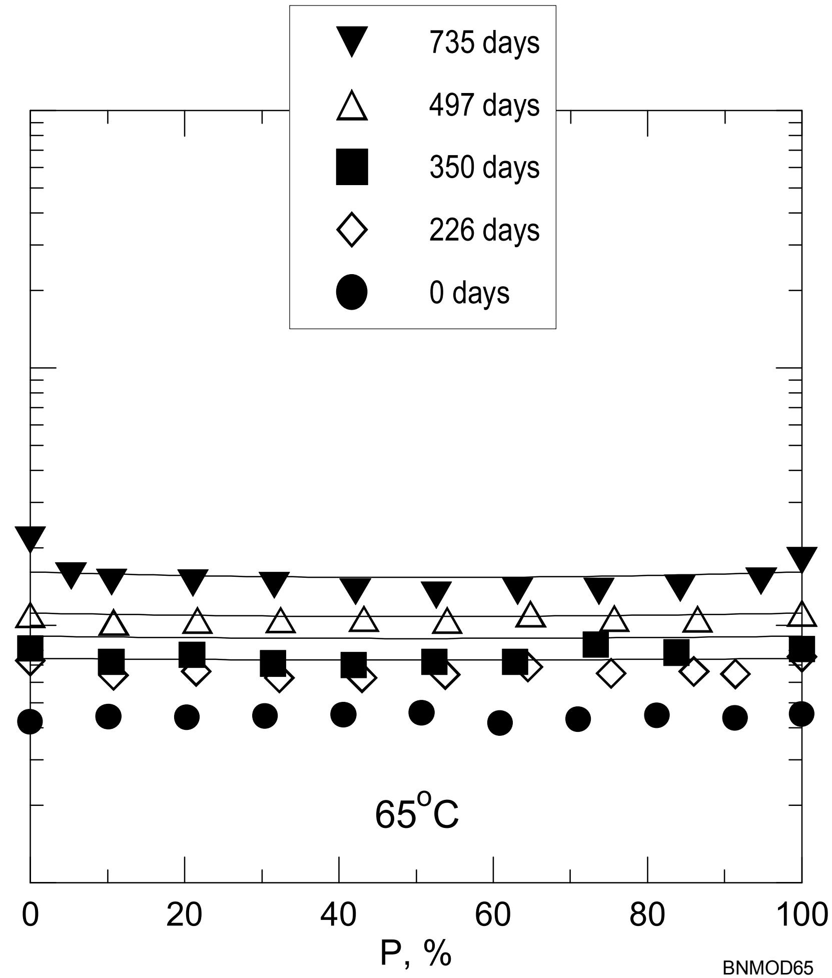
Gillen, K. T.; Clough, R. L.; Quintana, C. A. *Polym. Degrad. Stab., Modulus profiling of polymers 1987, 17, 31-47*

Modulus Profiler

Modulus Profiler Sample

Homogeneous Aging

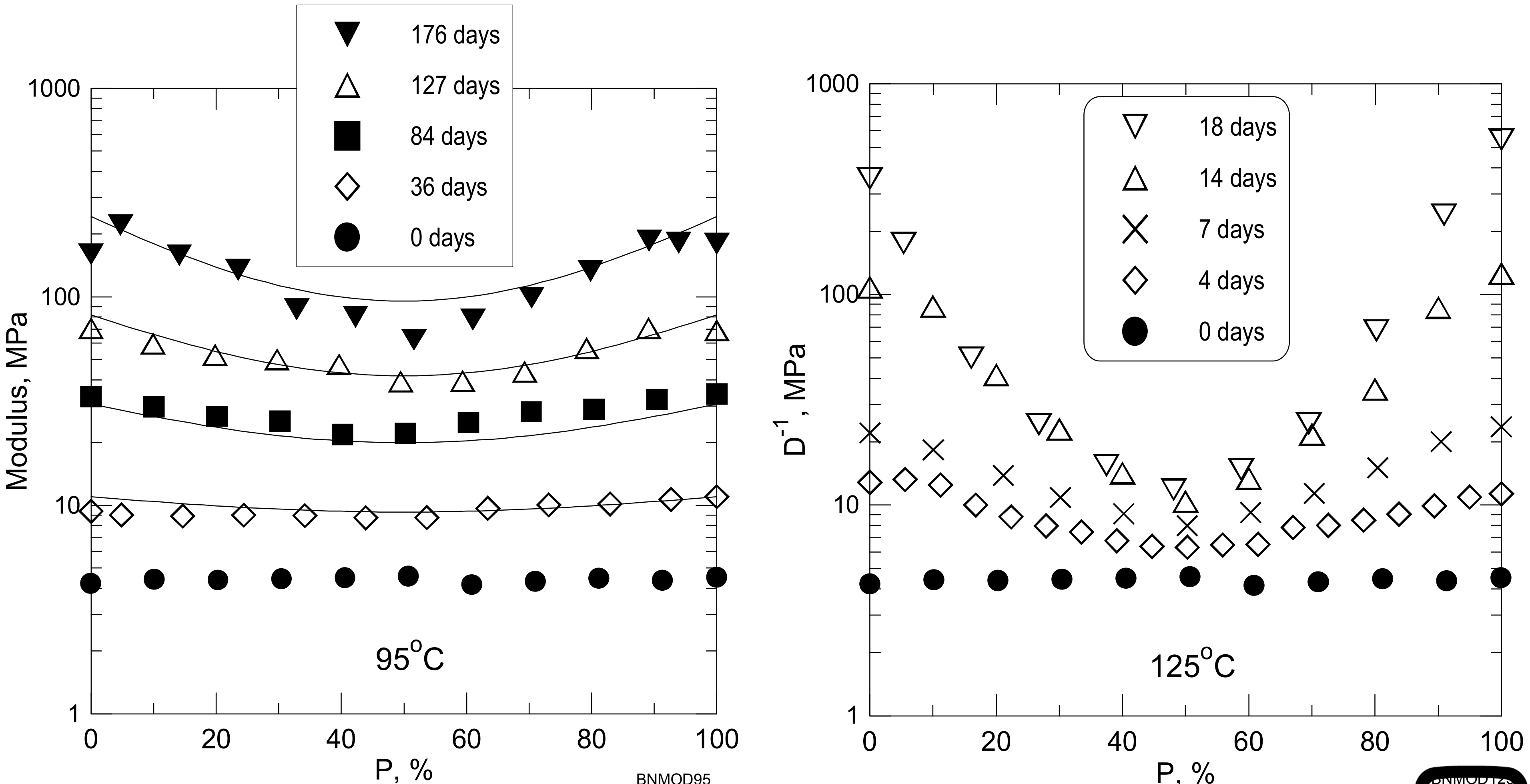
Modulus profiles of samples (nitrile rubber) aged at 65°C



Wise, J.; Gillen, K. T.; Clough, R. L. *Polymer Degradation and Stability, An ultrasensitive technique for testing the Arrhenius extrapolation assumption for thermally aged elastomers 1995, 49, 403-418.*

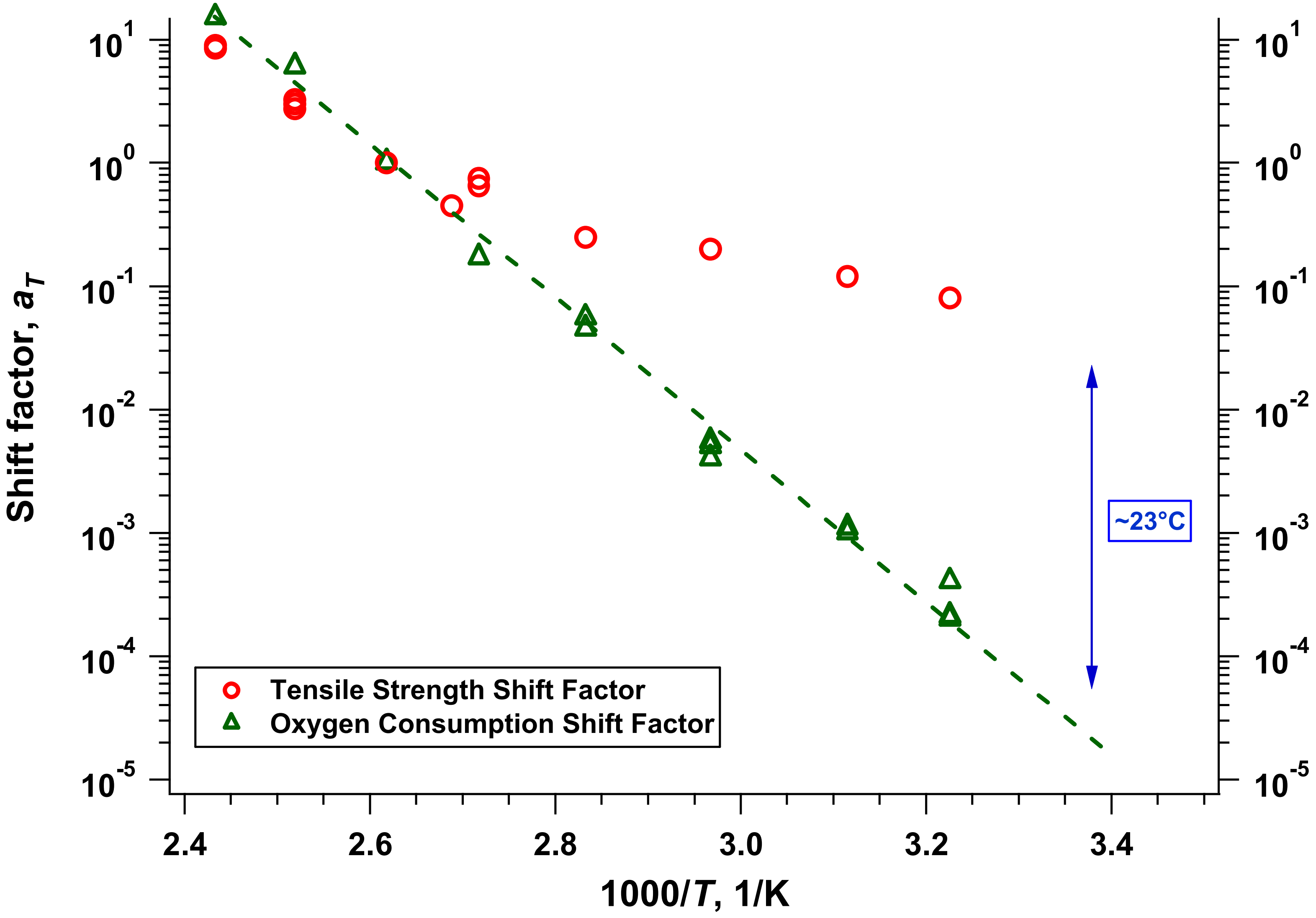
Heterogeneous Aging

Modulus profiles for samples aged at 95°C show that diffusion-limited oxidation (DLO) is becoming important; at 125°C, DLO effects are very significant



Wise, J.; Gillen, K. T.; Clough, R. L. *Polymer Degradation and Stability, An ultrasensitive technique for testing the Arrhenius extrapolation assumption for thermally aged elastomers 1995, 49, 403-418.*

Nylon: Tensile versus Oxygen Consumption



Thermal-oxidative tensile: Prediction vs. Experimental

Arrhenius Predictions

64 °C Thermal-oxidative

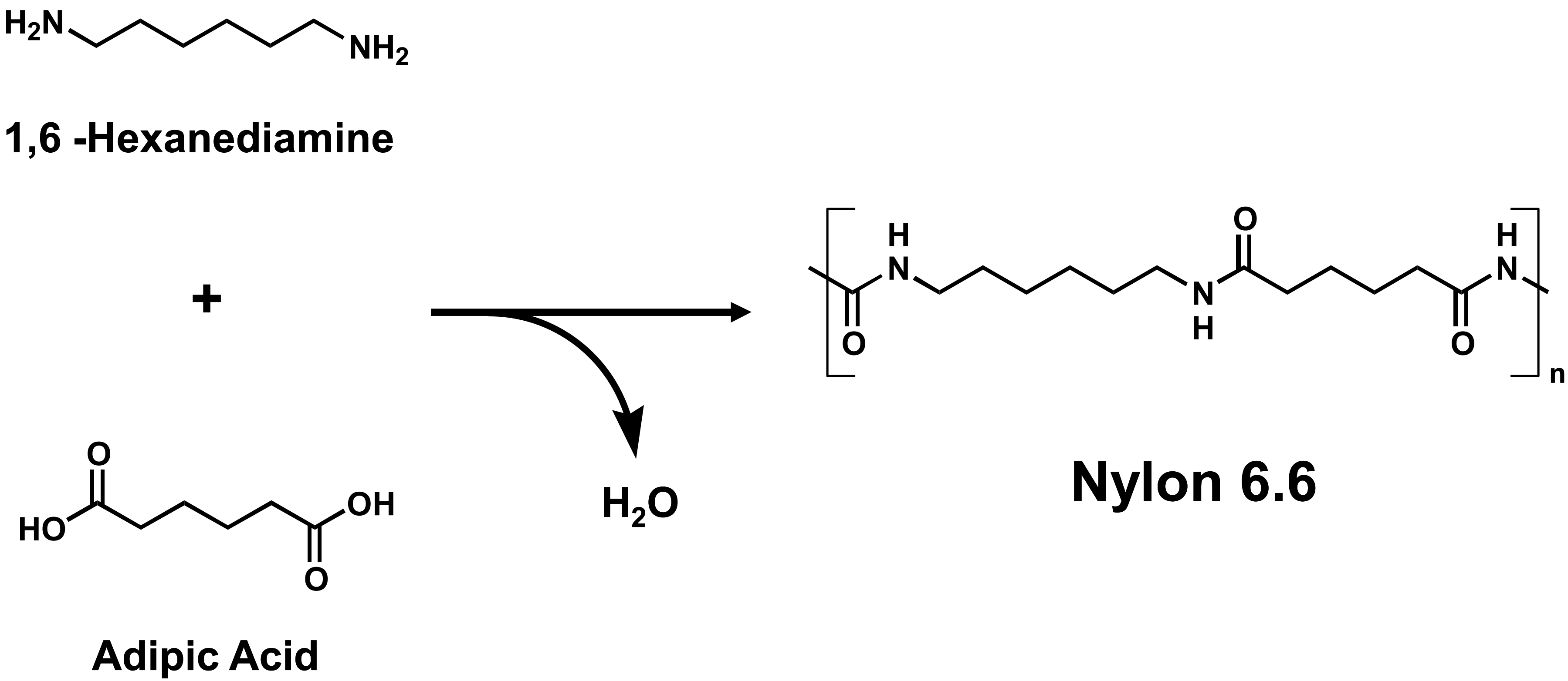
Arrhenius predictions severely off target suggest change in mechanism/non-Arrhenius behavior

Initial data Predicted: 92% at ca. 3700 days
Observe: 92% at ca. 835 days

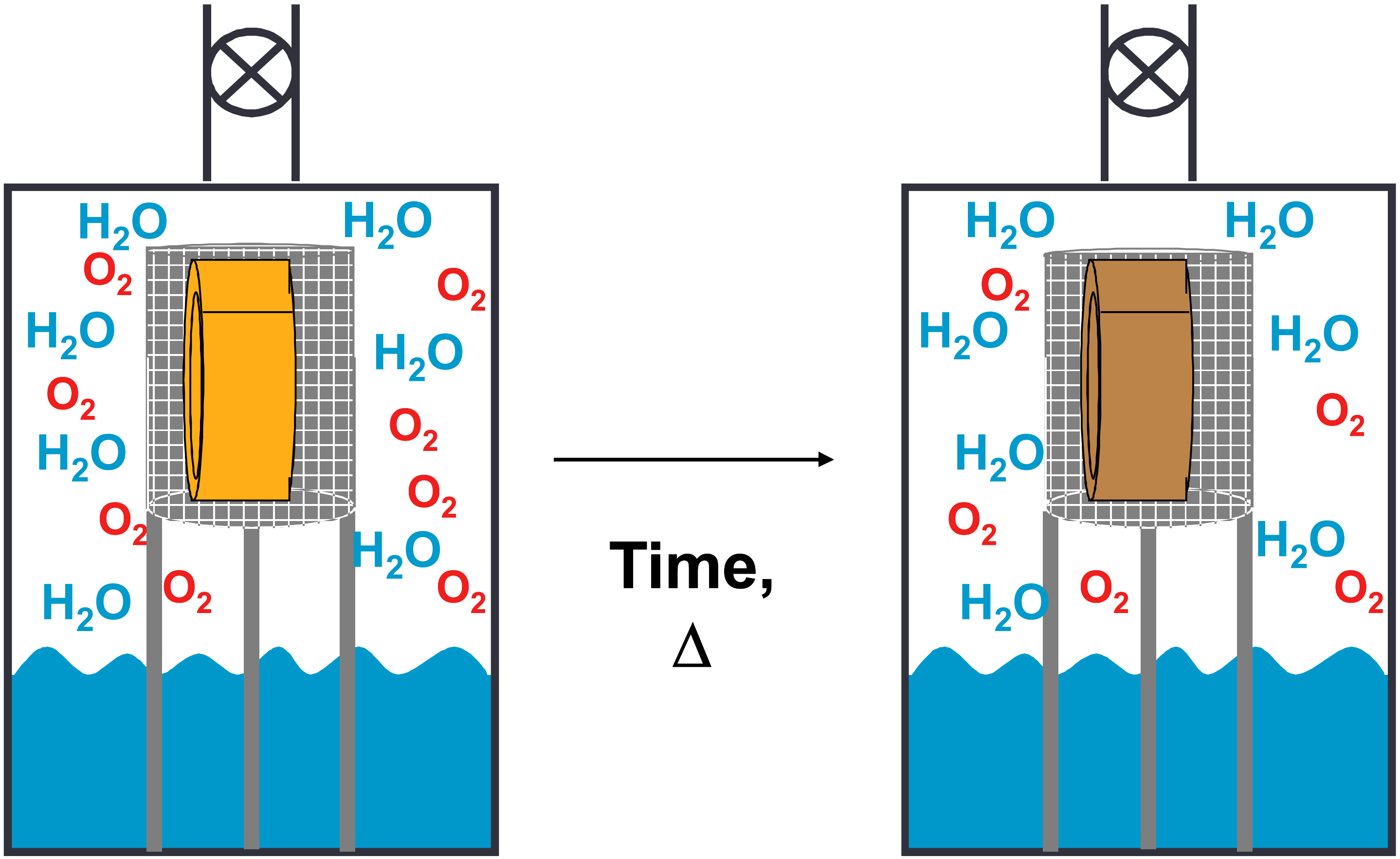
Oxygen consumption suggests no change in thermal-oxidative mechanism

Possible explanation involving mechanism change?

Nylon Structure



Humidity Aging Schematic



Humidity Aging Hardware

Nylon Program

External Publications

Bernstein, R.; Derzon, D. K.; Gillen, K. T., Nylon 6.6 accelerated aging studies: thermal-oxidative degradation and its interaction with hydrolysis. *Polymer Degradation and Stability 2005, 88 (3), 480-488.*

Bernstein, R.; Gillen, K. T., Nylon 6.6 accelerating aging studies: II. Long-term thermal-oxidative and hydrolysis results *Polymer Degradation and Stability 2010, 95 (9), 1471-1479.*

Published Several Polymer Preprints (American Chemical Society)

Currently Working on Kevlar Paper

Internal Publications

Bernstein, R.; Derzon, D. K.; Whinery, L. D.; Shedd, M. M.; Gillen, K. T. *Parachute Aging Studies; Nylon and Kevlar; SAND2008-6540; 2008.*

Report is Official Use Only/Export Controlled Information

Organic Materials Aging and Degradation

Specifics -o-rings
General path –most organic materials

This talk –details not important (all published)

O-ring Published Documentation

Bernstein, R.; Gillen, K. T. Polymer Degradation and Stability, Predicting the Lifetime of Fluorosilicone O-rings 2009, 94, 2107-2133.

Bernstein, R.; Gillen, K. T. "Fluorosilicone and Silicone O-Ring Aging Study," SAND2007-6781, Sandia National Laboratories, 2007.

Chavez, S. L.; Domeier, L. A. "Laboratory Component Test Program (LCTP), Stockpile O-Rings," BB1A3964, 2004.

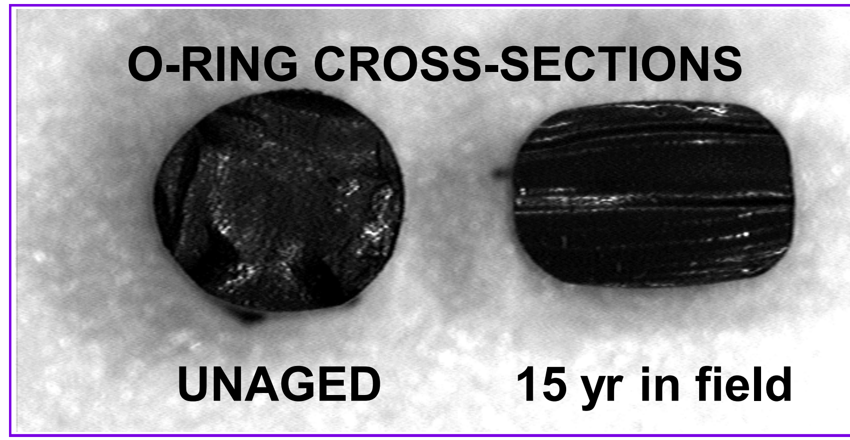
Gillen, K. T.; Bernstein, R.; Wilson, M. H. *Polymer Degradation and Stability,* Predicting and Confirming the Lifetime of O-rings 2005, 87, 257-270.

Gillen, K. T.; Celina, M.; Bernstein, R. In *Polymer Degradation and Stability* Validation of Improved Methods for Predicting Long-Term Elastomeric Seal Lifetimes from Compression Stress-Relaxation and Oxygen Consumption Techniques, 2003; Vol. 82, pp 25-35.

O-rings Background

Used as environmental seals or other seals

Most systems filled with inert gas to protect interior components from oxidation & hydrolysis



Previously:

No technique to measure equilibrium sealing force

No technique to rapidly achieve equilibrium compression set

No correlation

CSR Jigs

Gap of jig can be adjusted to any desired size

O-ring pieces cut to allow air circulation

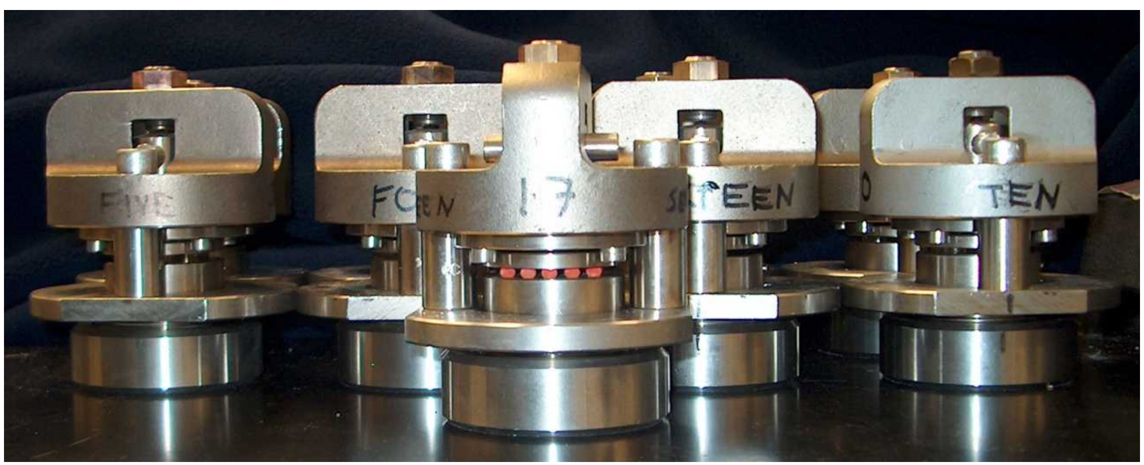
Measurement of force involves very slow and slight compression until electrical contact is broken between the top and bottom plates

Jigs can be placed in ovens, thus providing isothermal measurements

Compression Stress Relaxation (CSR)

Shawbury-Wallace Compression Stress Relaxometer (CSR) MK II

Commercial Instrument
Measure of Force
-O-ring sealing force
Can Adjust Gap Size to Approximate Actual Compression in System



(Wallace Test Equipment, Cryodon, England)

Accelerated aging

1) Physical force decay

-Equilibrium values achieved –starting point

-Ability to get field returned o-ring force –ending point

Not talking about in this presentation

2) Chemical force decay

Prediction of force changes as a function of aging

Accelerated aging

1) Physical force decay

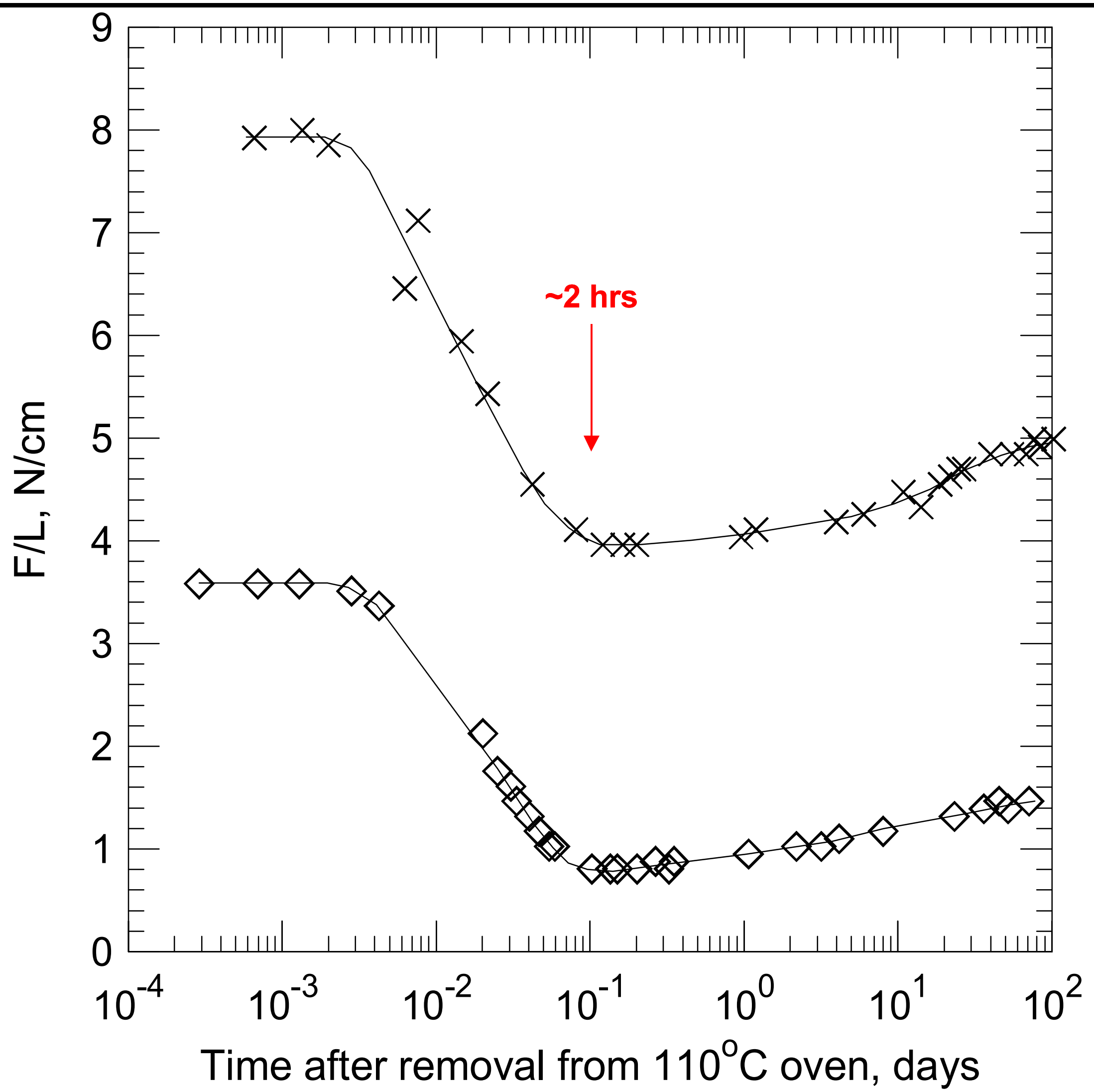
-Equilibrium values achieved –starting point

-Ability to get field returned o-ring force –ending point

2) Chemical force decay

Prediction of force changes as a function of aging

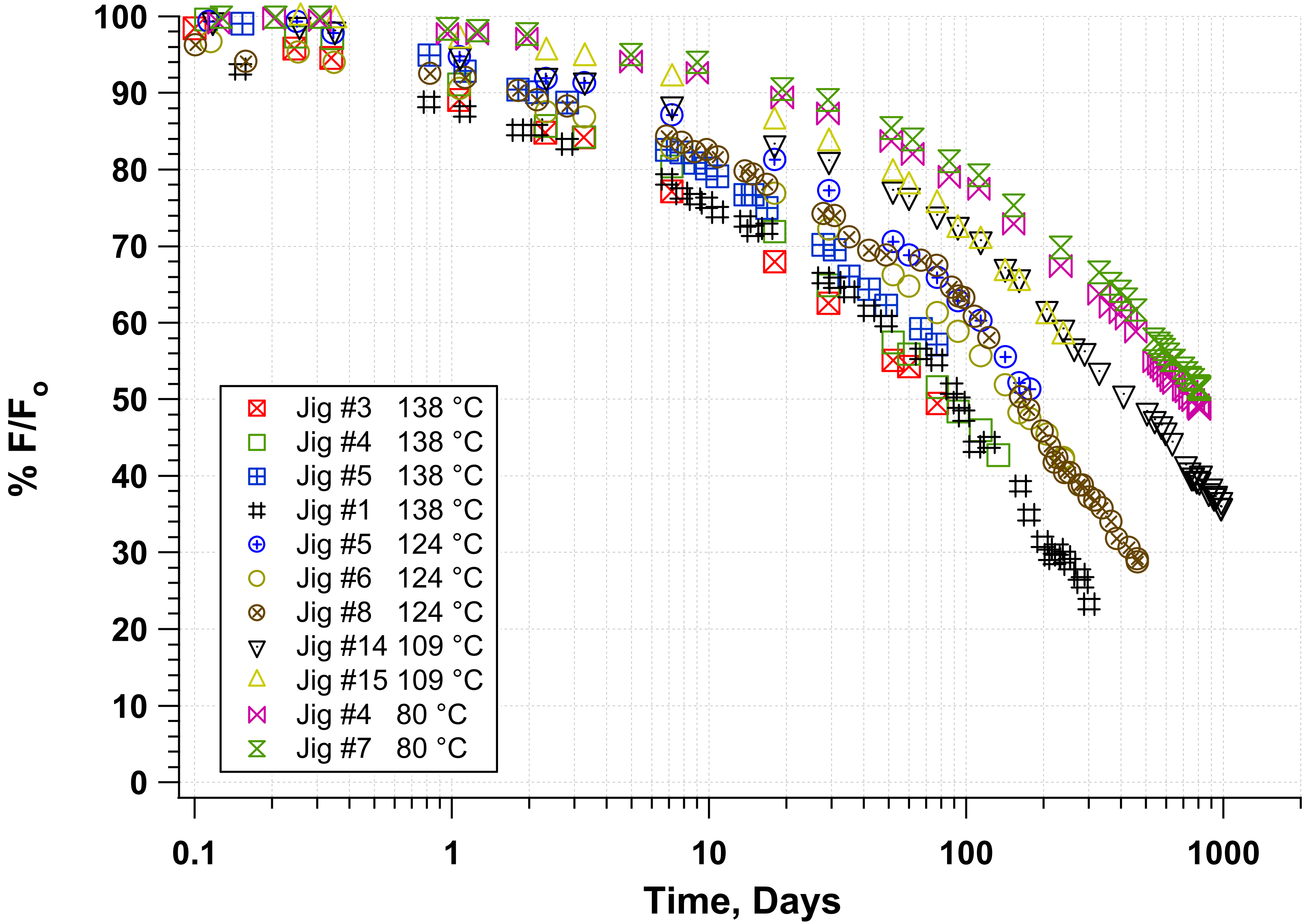
Why we do isothermal measurements…



Sealing force per unit length versus time out of a 110 °C oven for two CSR jigs containing Butyl-A o-ring segments that had aged under 25% compression until the force degraded by ~42% (top curve) and ~72% (bottom curve), respectively.

Gillen, K. T.; Celina, M.; Bernstein, R. In *Polymer Degradation and Stability* Validation of Improved Methods for Predicting Long-Term Elastomeric Seal Lifetimes from Compression Stress-Relaxation and Oxygen Consumption Techniques, 2003; Vol. 82, pp 25-35.

All Jigs at Temperatures -Fluorosilicone



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Time-Temperature Superposition

Does mechanism change as a function of temperature?

If same mechanism:

- same shape (log graph)
- should be constant acceleration (multiple)

1. Pick a reference temperature
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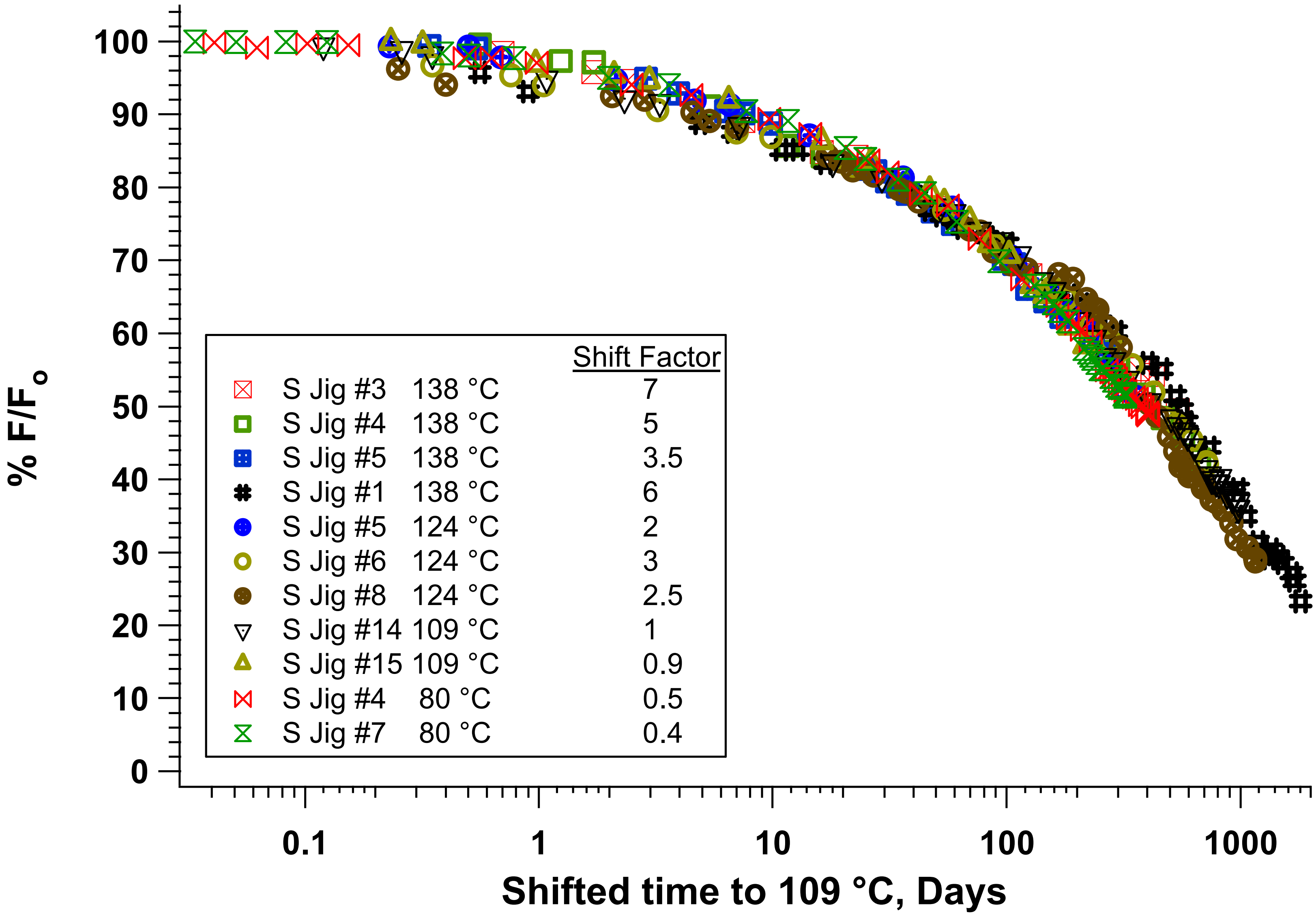
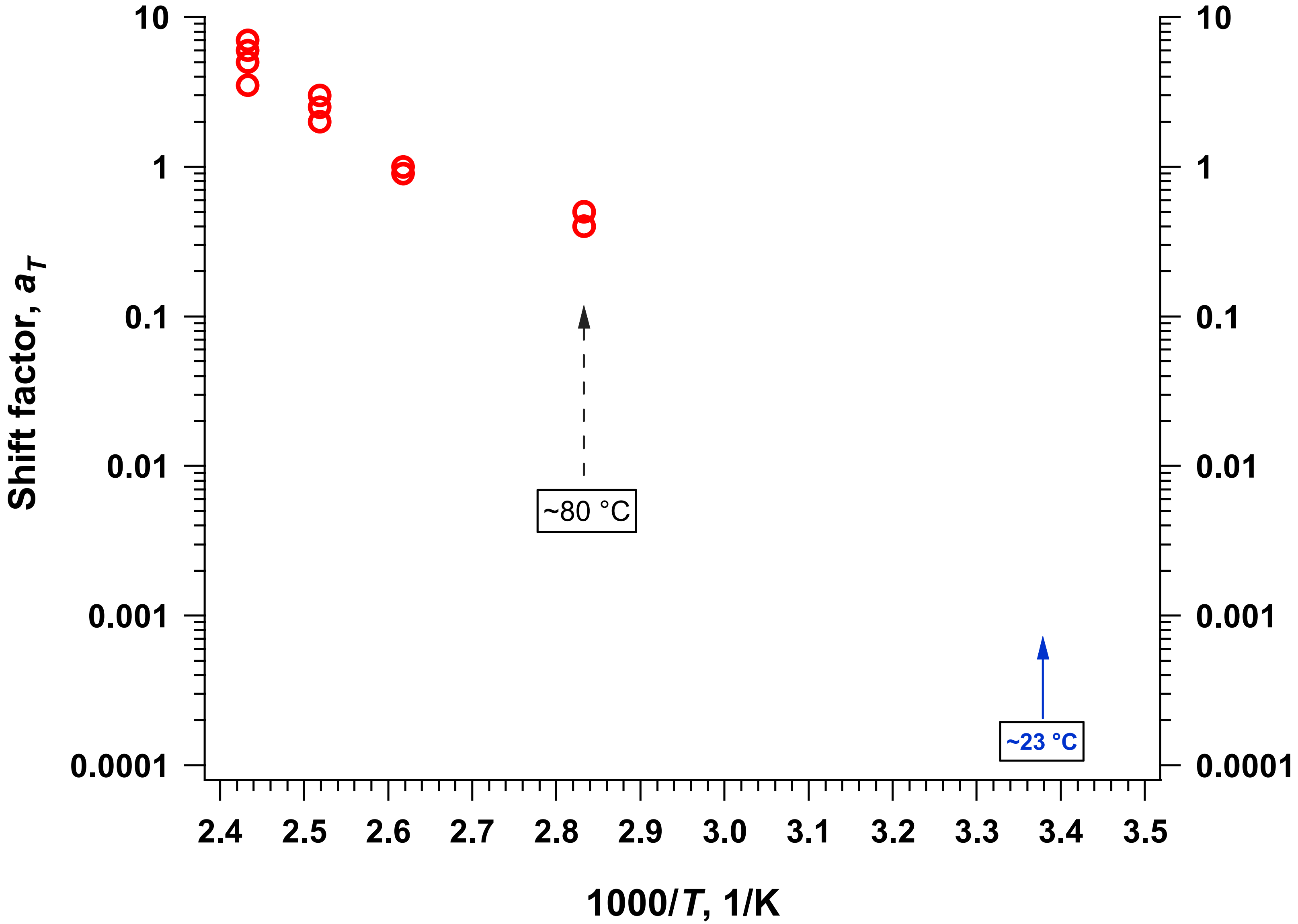
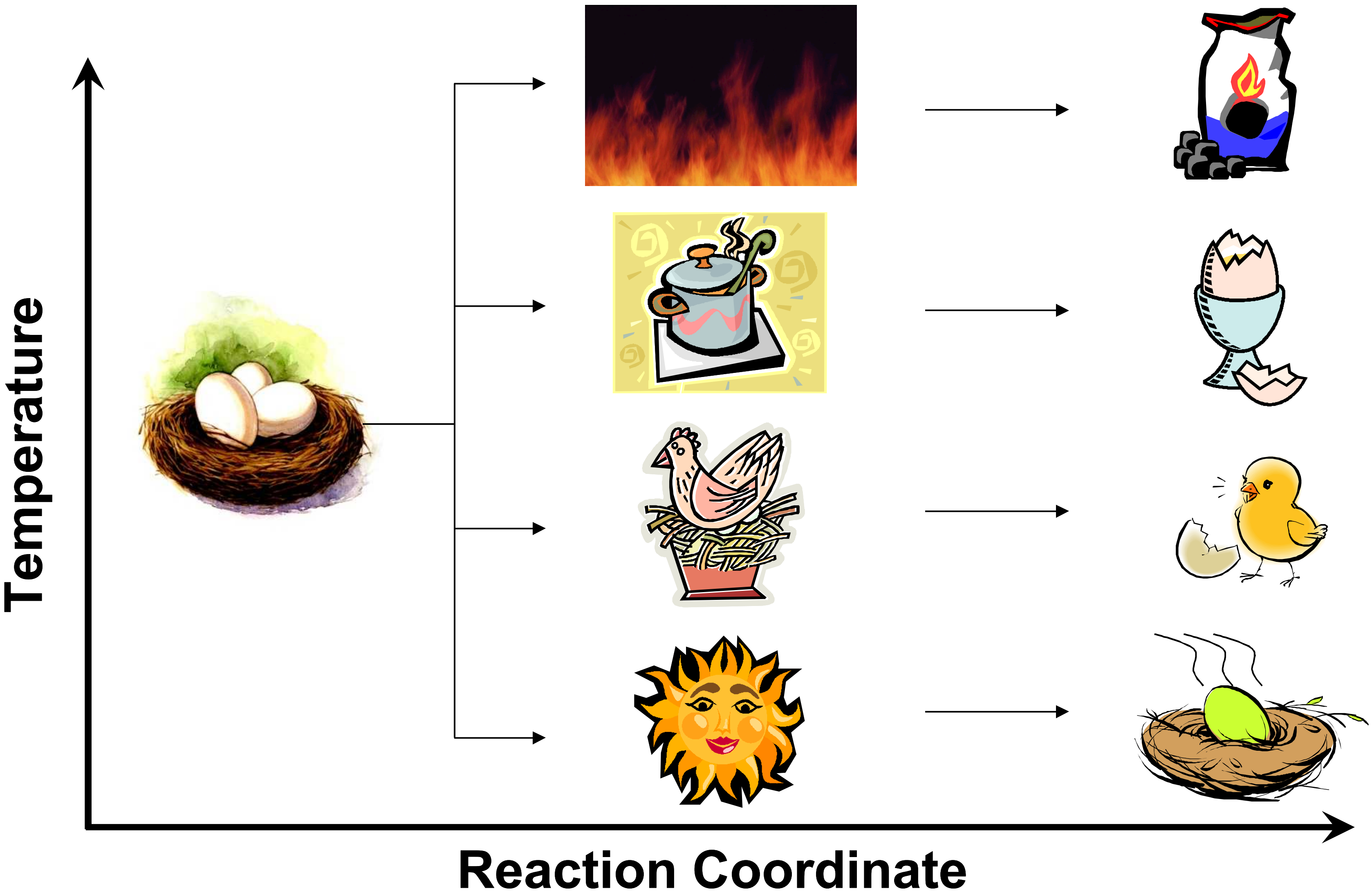
Time-Temperature Superposition



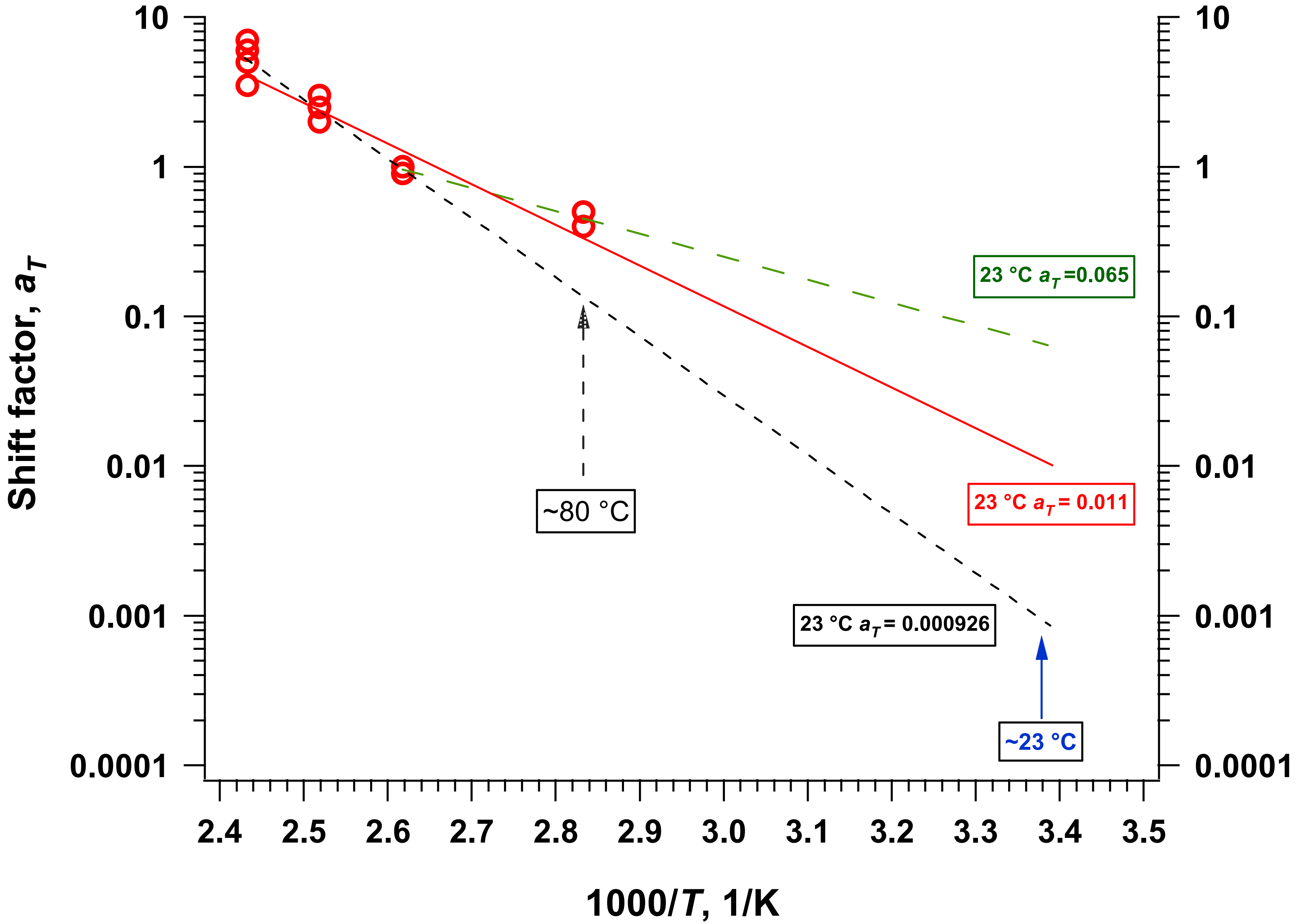
Shift Factor Plot



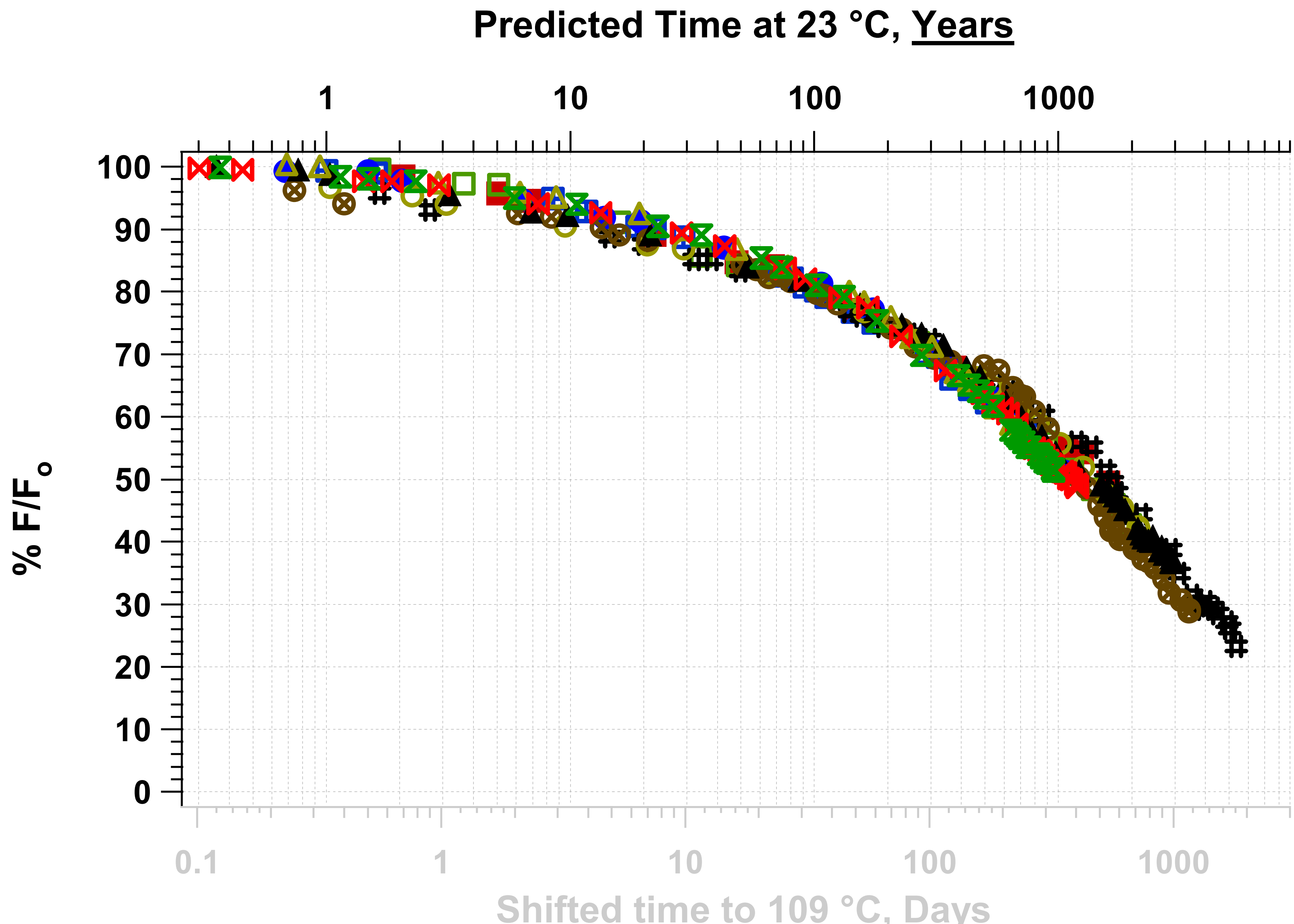
‘Accelerated Aging’



Shift Factor Plot



Shifted Data with RT 'Prediction' w/o 80 C data



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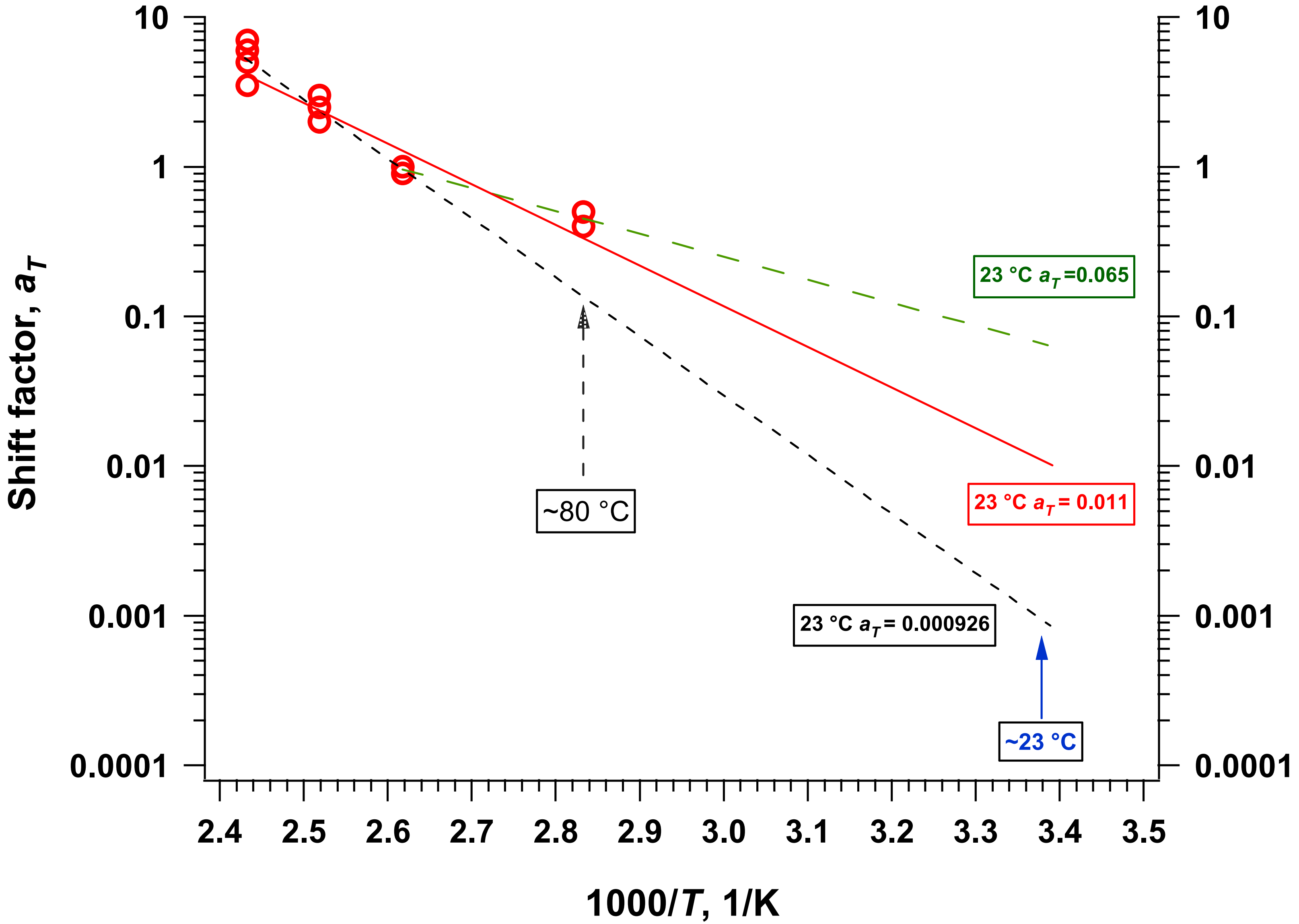
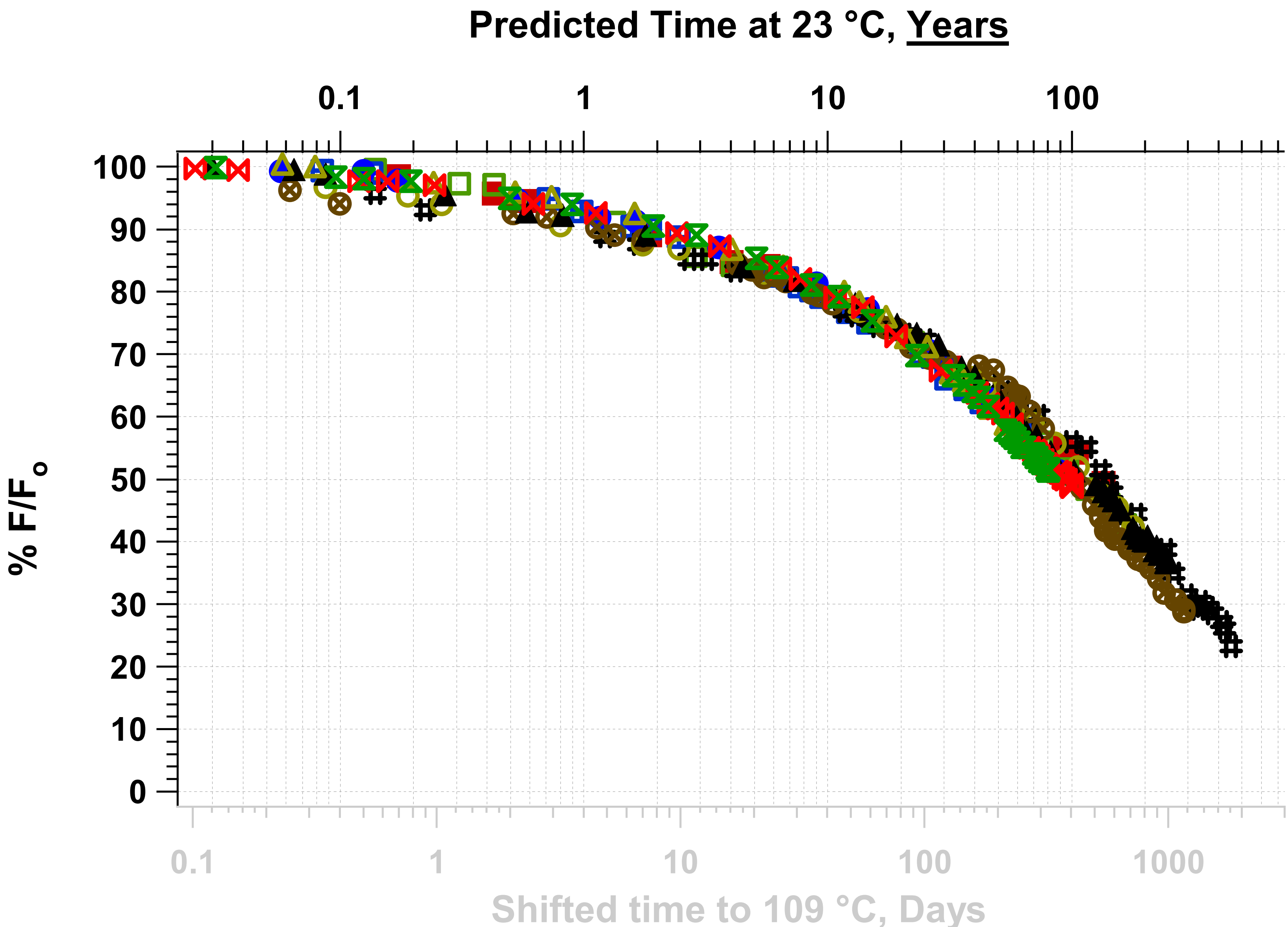
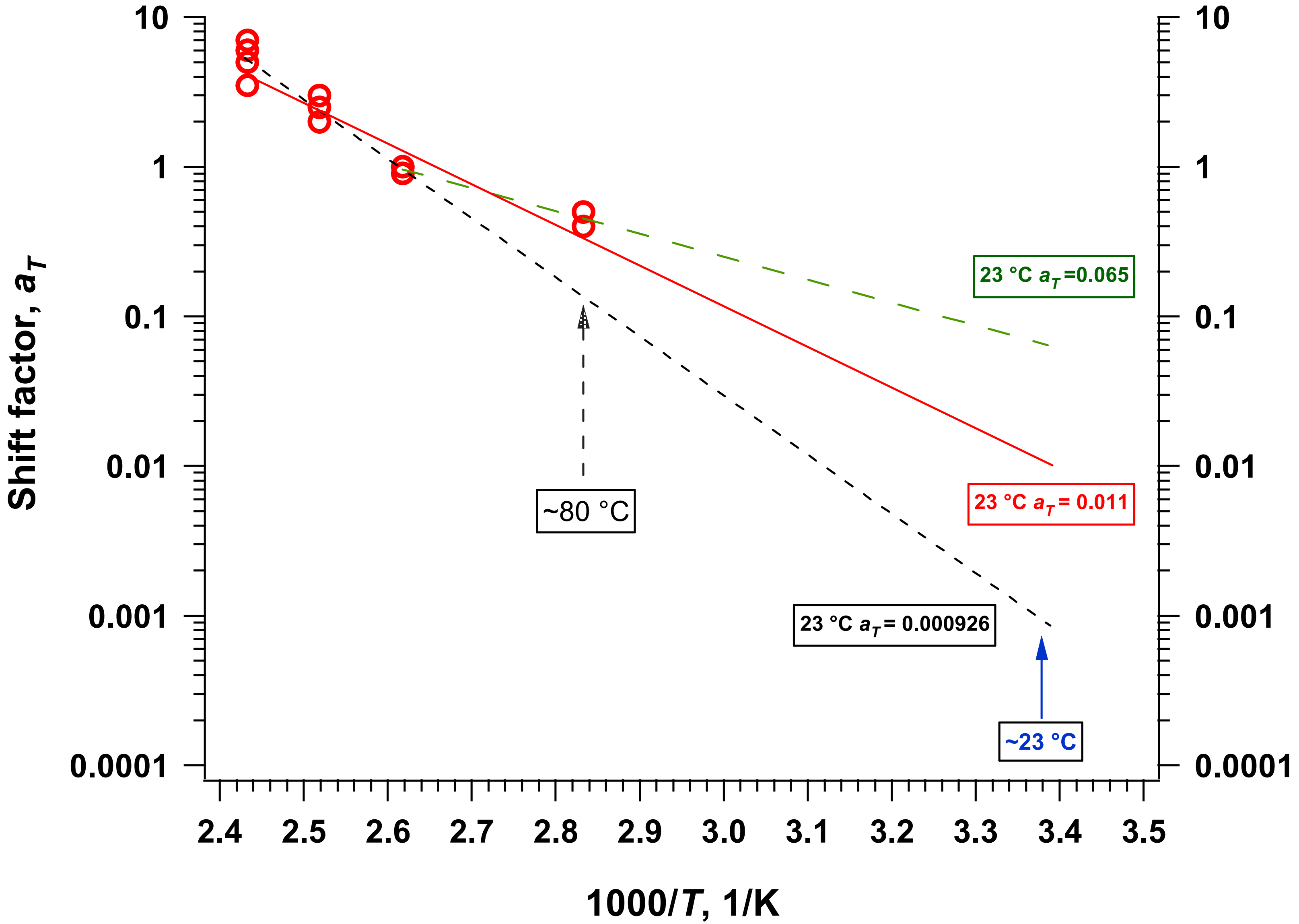


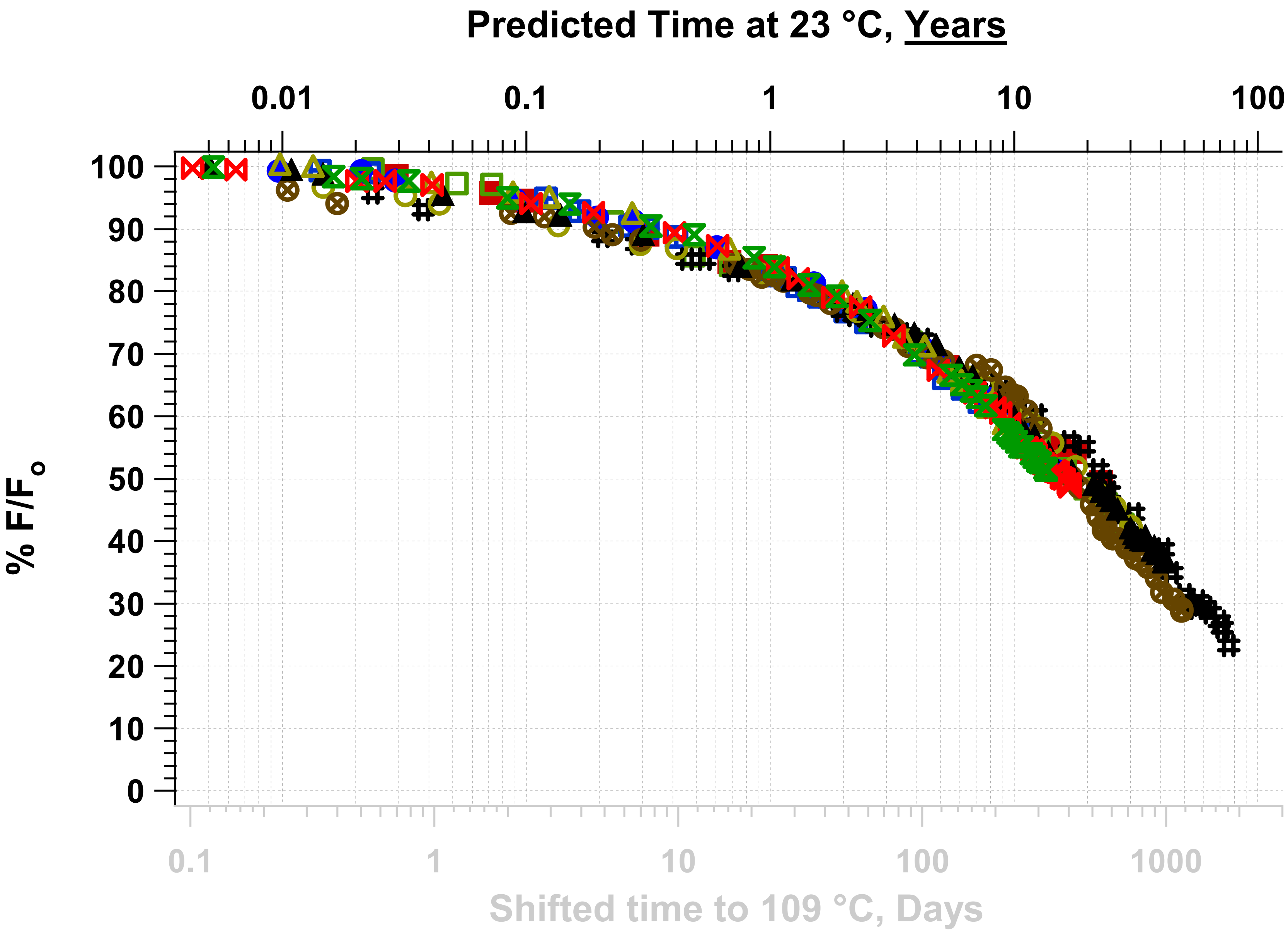
Shifted Data with RT 'Prediction' All data



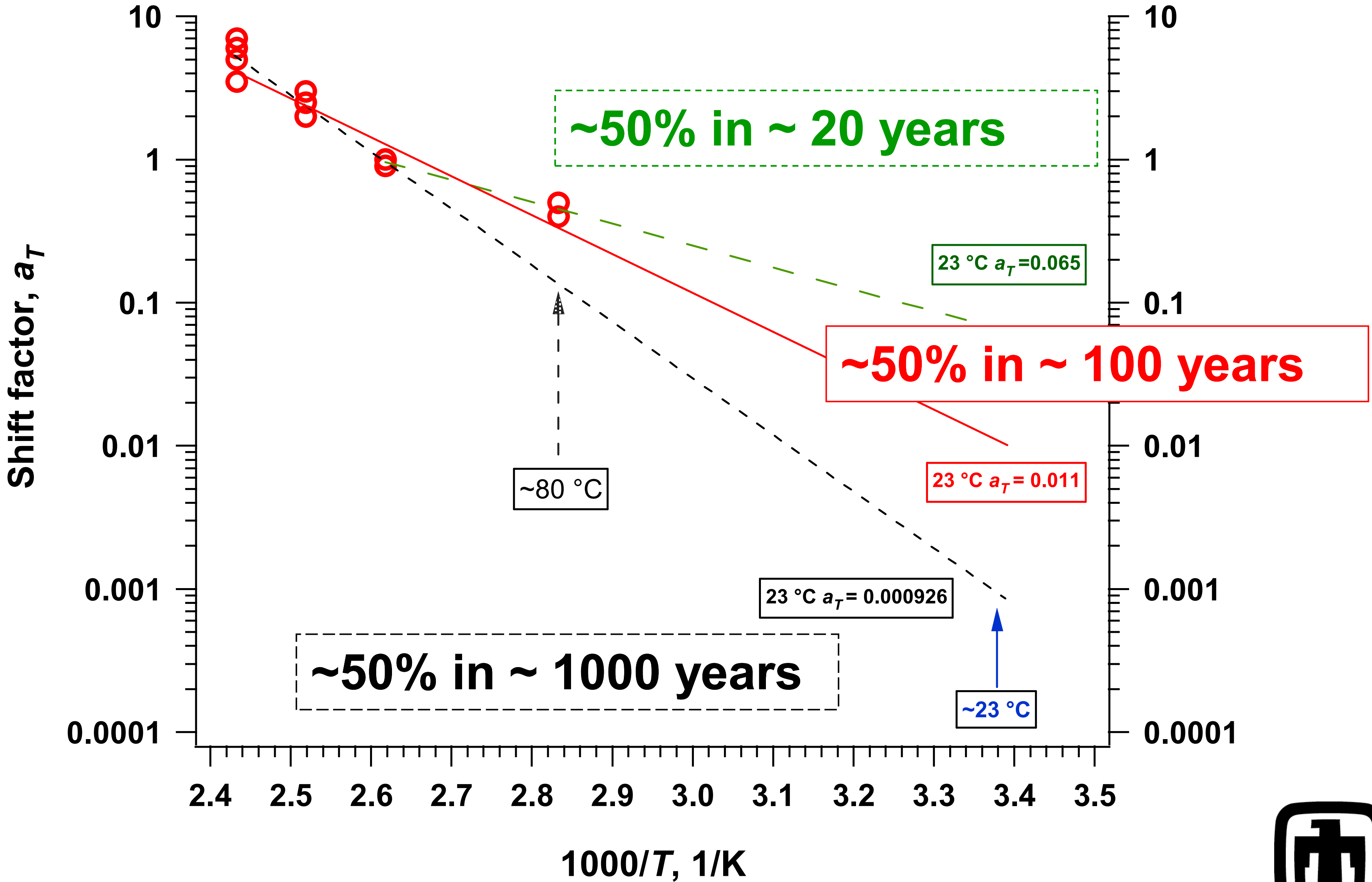
Shift Factor Plot



Shifted Data with RT 'Prediction' 109 and 80 only



Shift Factor Plot



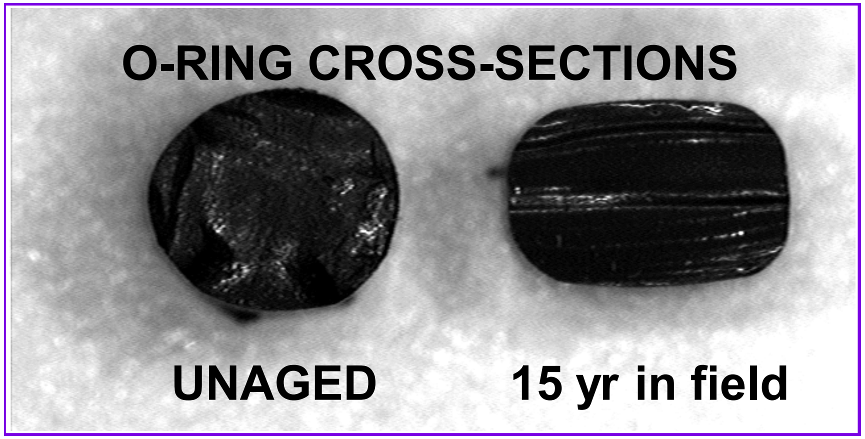
O-rings

Sealing force arguably most important parameter

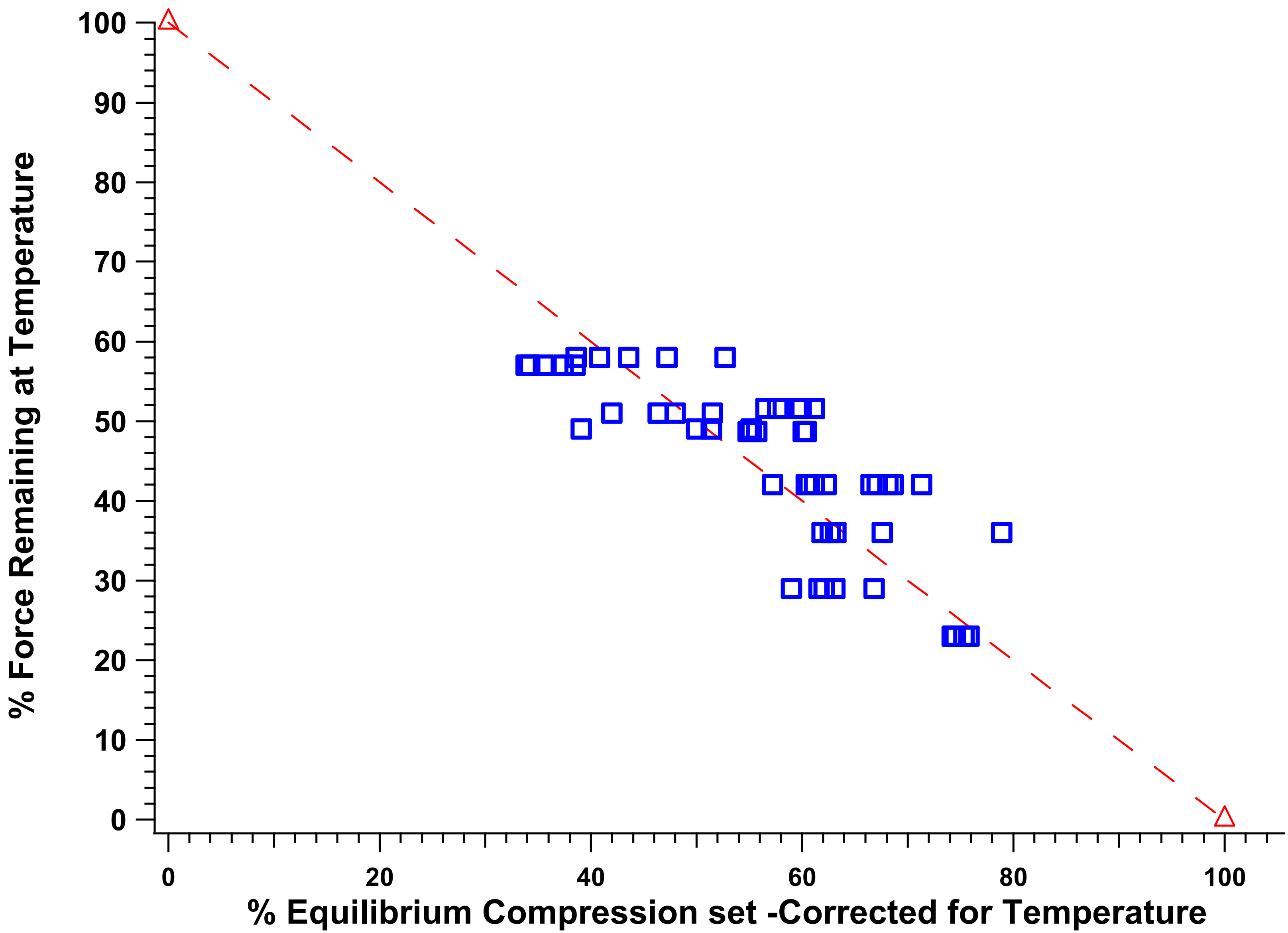
Correlation between equilibrium values

sealing force ⟷ **compression set**

sealing force	compression set
Difficult to measure slow and laborious	Easy to measure quick and simple

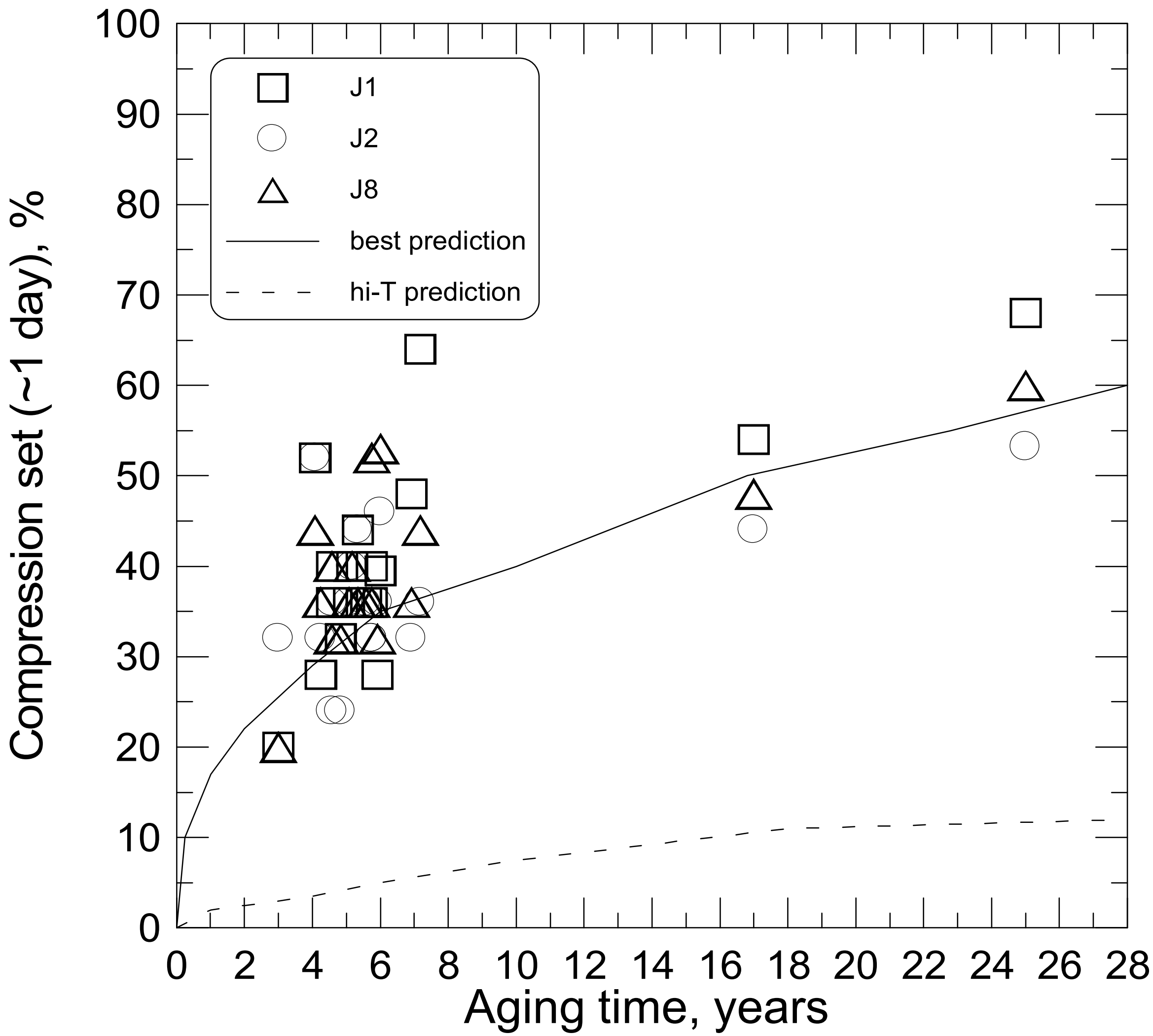


Force versus Compression Set Data -Fluorosilicone



Field Data*

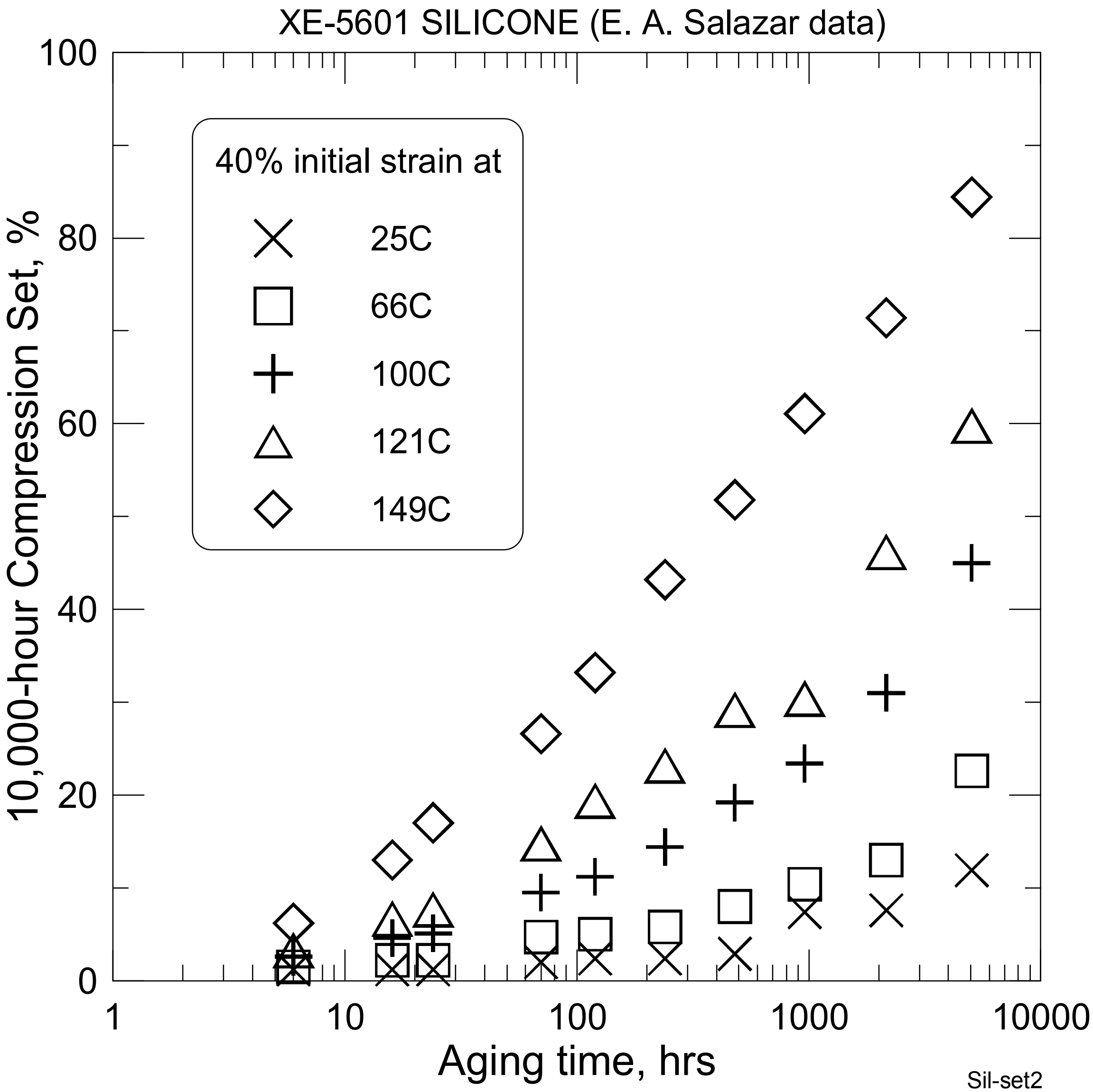
*** not quite the whole story, but good enough for this conversation!**



Compression set measurements of three fluorosilicone o-rings taken on surveillance units approximately 1 day after removal from the unit. The solid curve and the dashed curve assume a linear relationship between set and force decay.

Bernstein, R.; Gillen, K. T. ***Polymer Degradation and Stability, Predicting the Lifetime of Fluorosilicone O-rings 2009, 94, 2107-2133***

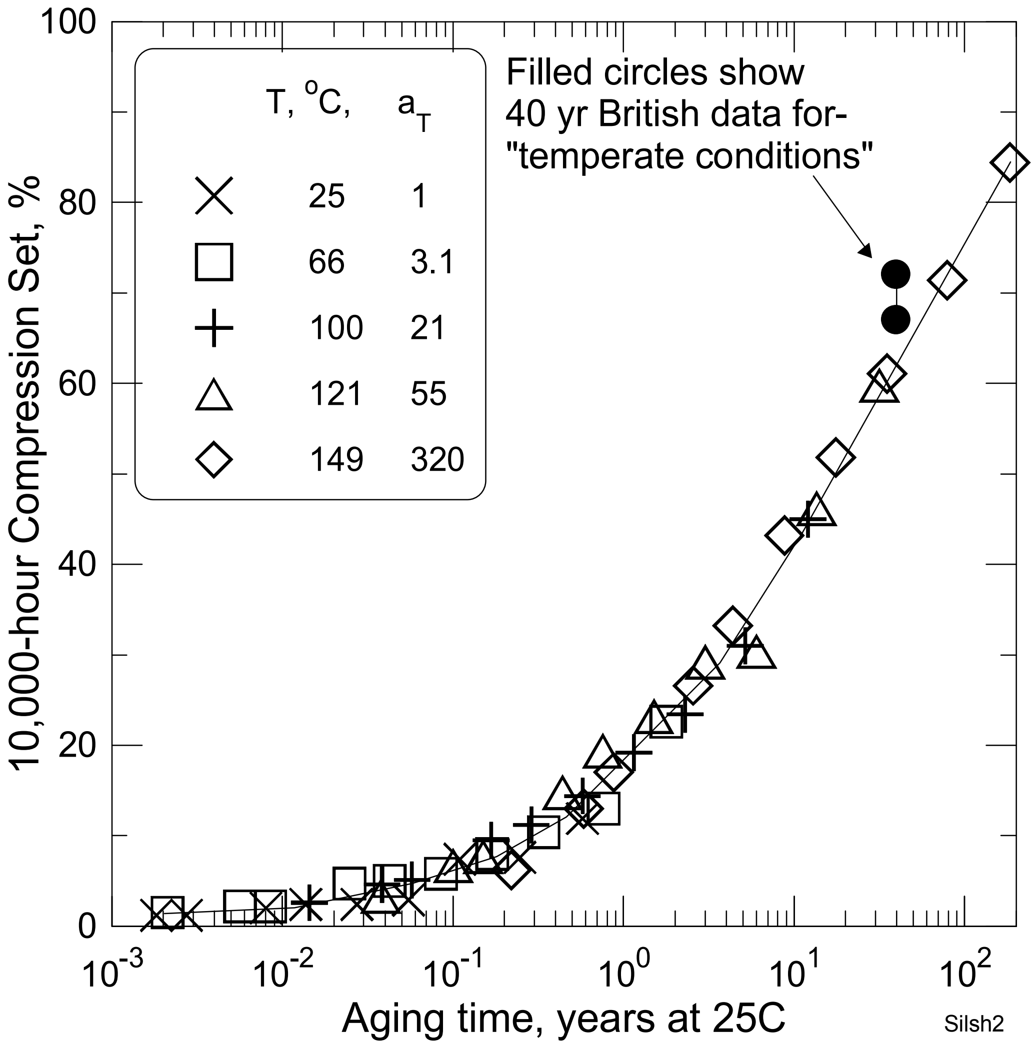
Other Compression Set Data



Different Silicone
Different Program
Different PI

Gillen, K. T. "Silicone seal analysis," Internal Memo, SNL, 2001.

Compression Set

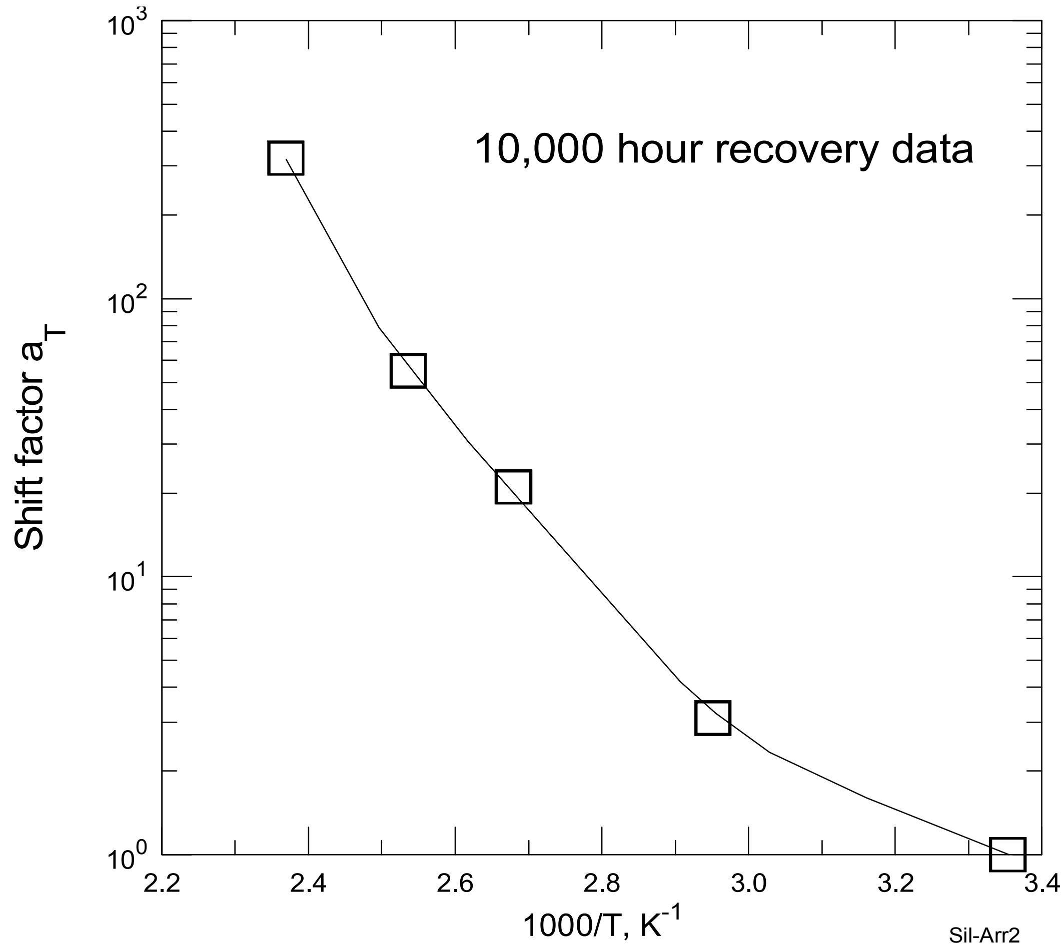


Data Analyzed by Gillen

Added in 40 year RT data from another source

Gillen, K. T. "Silicone seal analysis," Internal Memo, SNL, 2001.

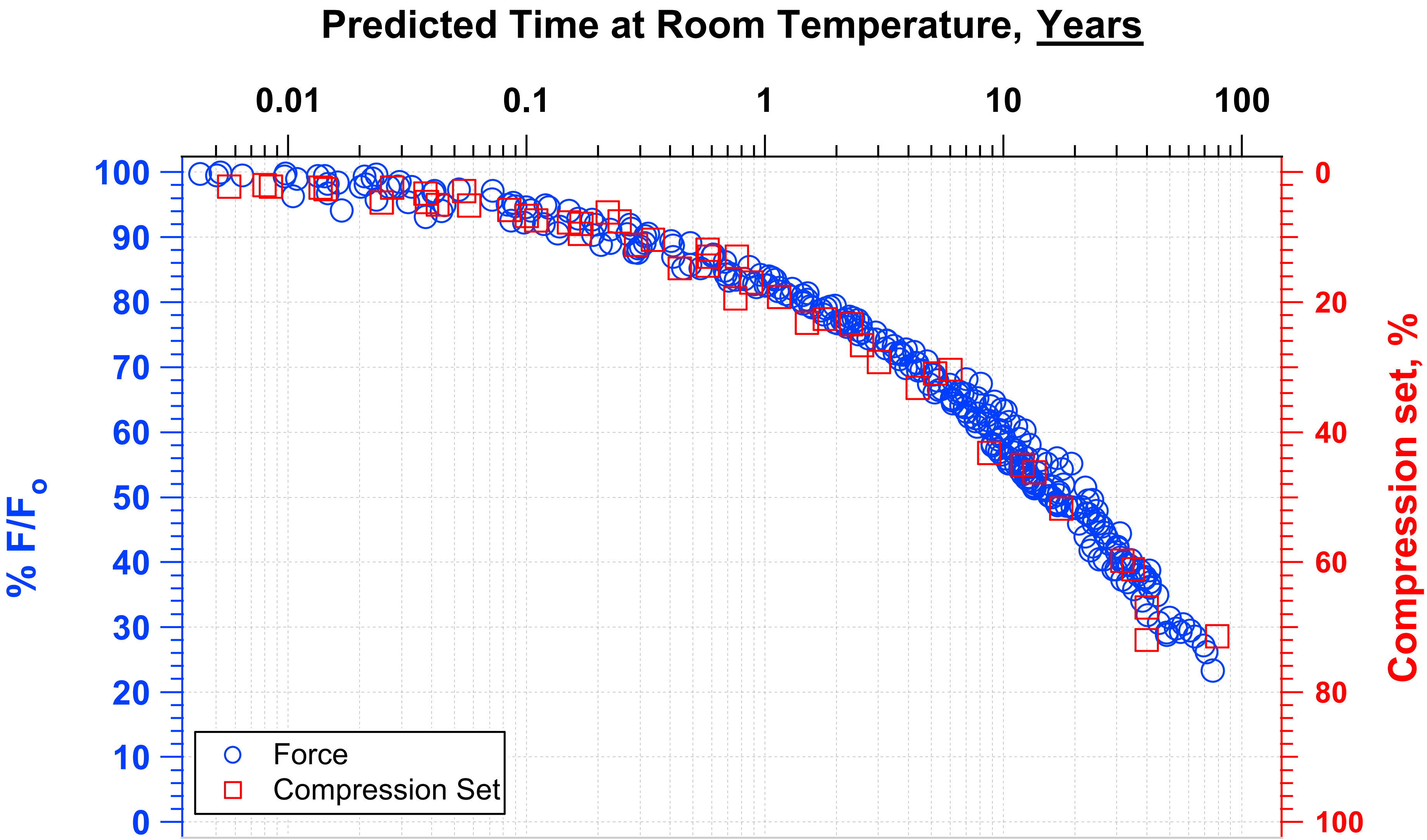
Arrhenius Plot for Compression Set



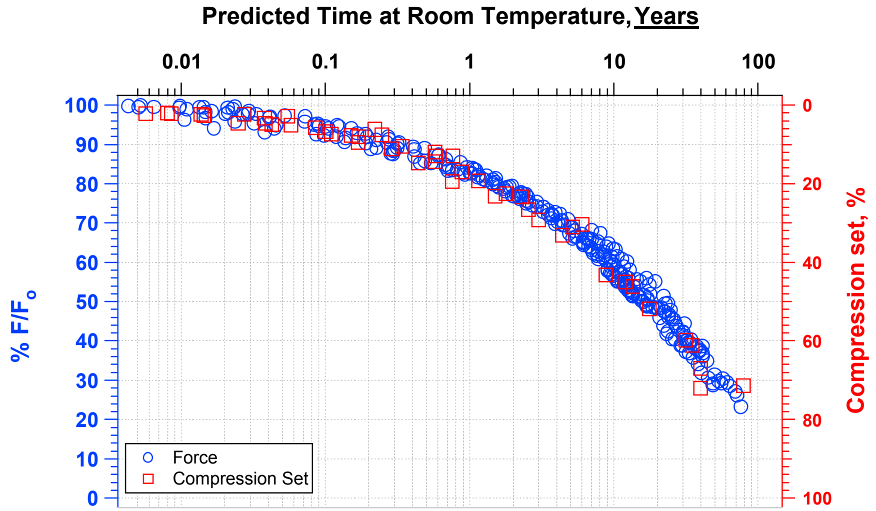
Arrhenius plot of the shift factors for silicone compression set which leads to an aging room temperature prediction for compression set

Gillen, K. T. "Silicone seal analysis," Internal Memo, SNL, 2001.

Force versus Compression Set Data



Force versus Compression Set Data

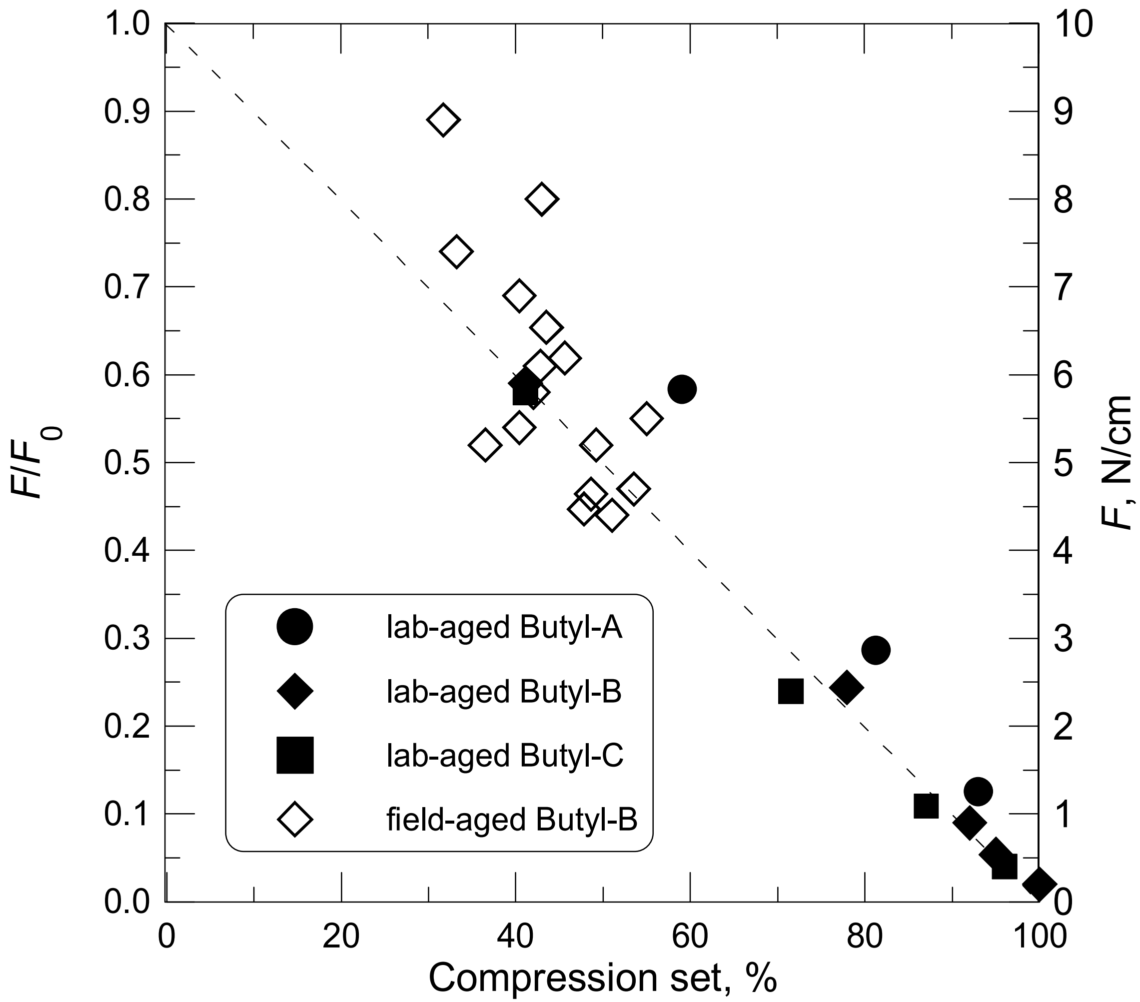


Correlation between current Silicone Force data and Compression set data obtained from *three different sources (and different sizes!)*

Fluorosilicone versus Silicone!!

Displays confidence in generalized predictions about silicone o-rings state of health (CS easy to measure) under oxidative environments*

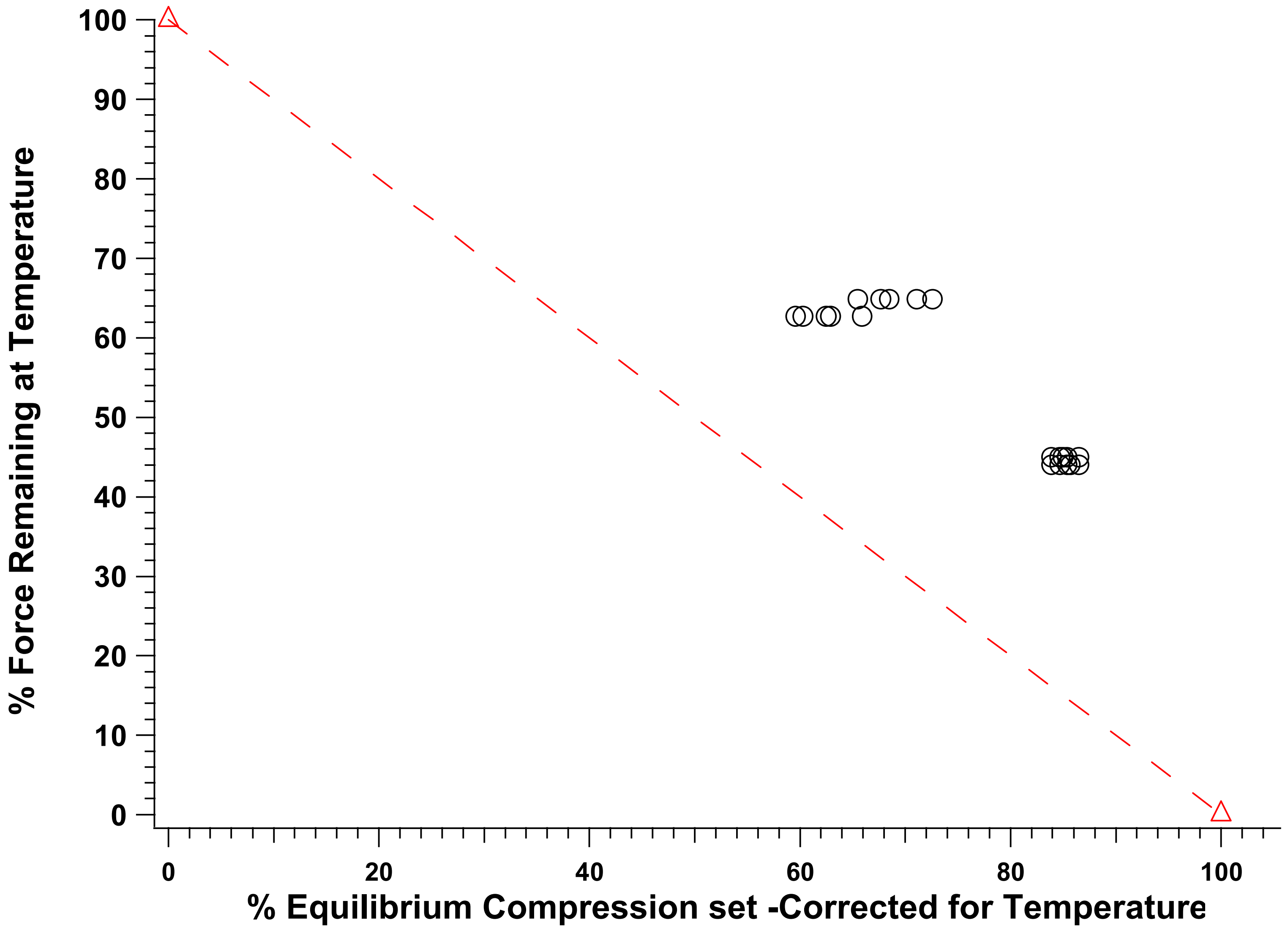
Butyl Force vs. Compression set; lab and field aged



Equilibrium values of compression set plotted versus F/F_0 for laboratory-aged o-rings for three butyl materials plus field results for Butyl-B plotted assuming that F_0 = 10 N/cm.

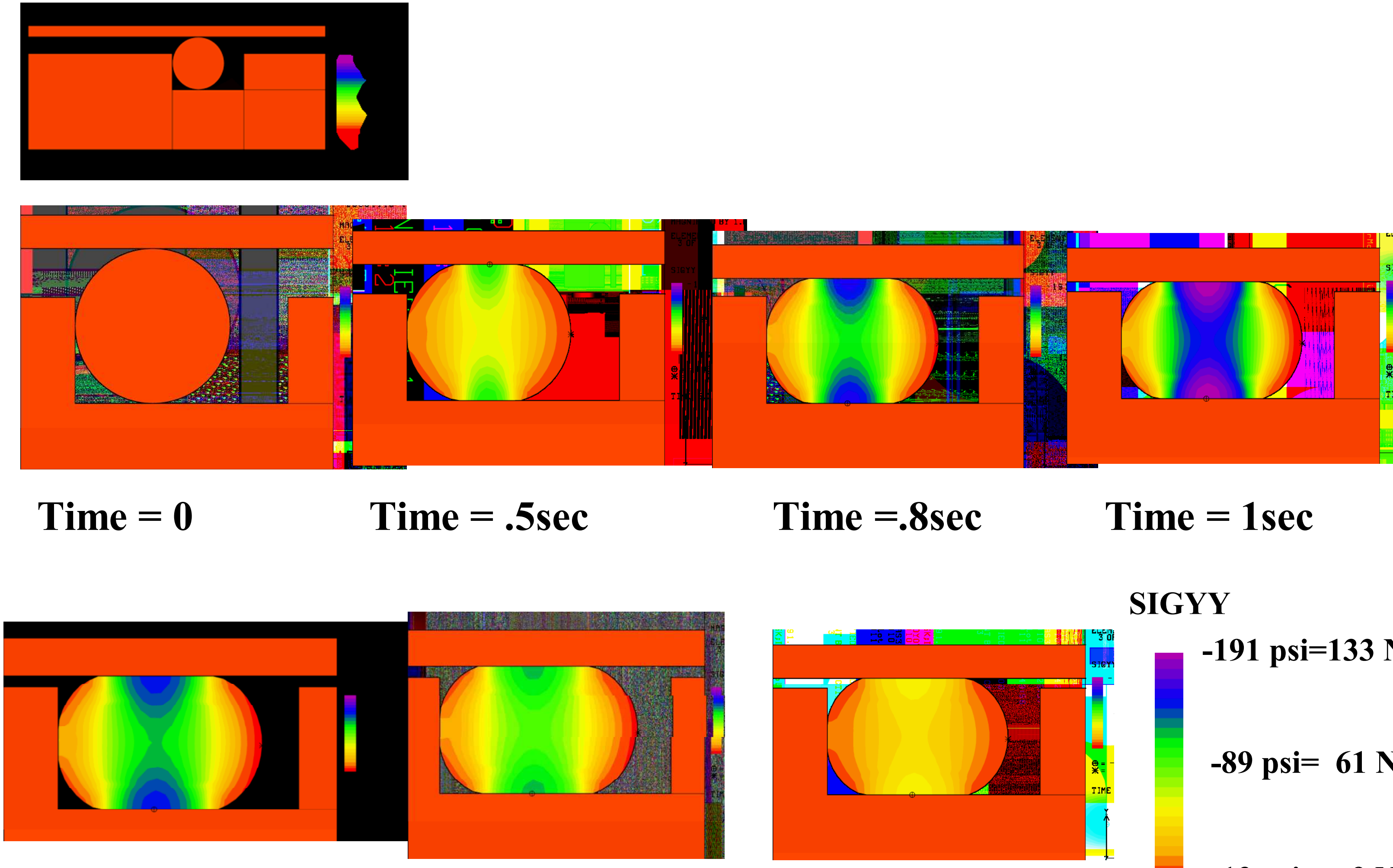
Gillen, K. T.; Bernstein, R.; Wilson, M. H. *Polymer Degradation and Stability,* Predicting and Confirming the Lifetime of O-Rings 2005, *87*, 257-270.

Heavily Filled Silicone



Conducting o-rings compression set versus force remaining

Progression of Stress Relaxation due to Chemical Aging



Slide Courtesy of David Lo

Take home messages…

1) Be aware of mechanism changes
2) Understand chemistry/be careful with the details
   –DLO, O_2 vs. H_2O etc
3) Find something to measure
4) Do things at many temp (as far apart as possible)
5) Do things for very *very* long time
6) Validate against real world

7) It would be nice to know *your* performance requirements

Lots of help…

Dora Derzon, Brad Hance, Don Bradley, Roger Assink, James Hochrein, Steven Thornberg, David Lo, Kathy Alam, Laura Martin, John Schroeder, Patti Sawyer, Mark Stavig, and Ken Gillen

What are your thoughts?

What are your tricks of the trade?

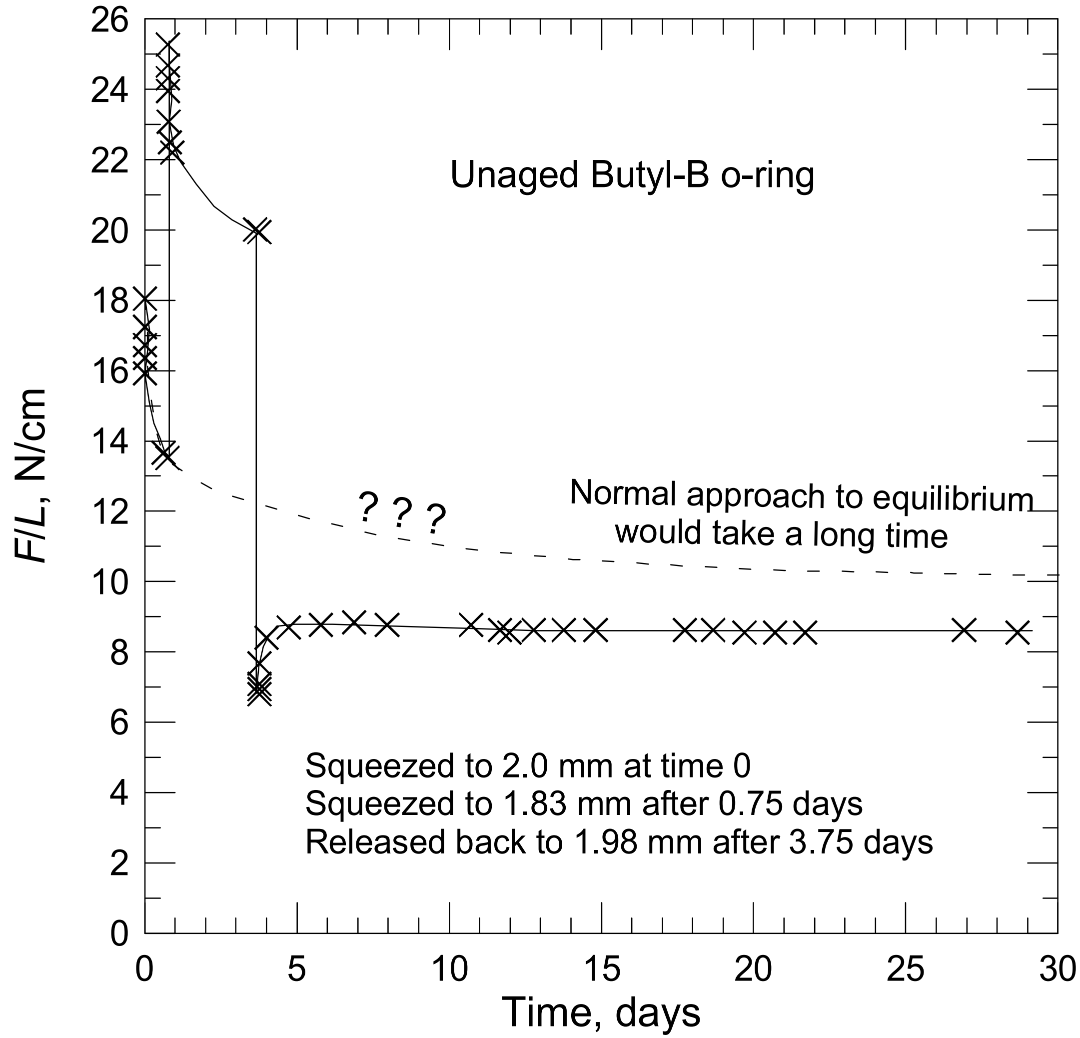
What are your concerns?

What are your strength/weaknesses with regard to organic materials aging techniques?

Can we foster a collaboration? Annual meetings?

Questions…

Over-compression

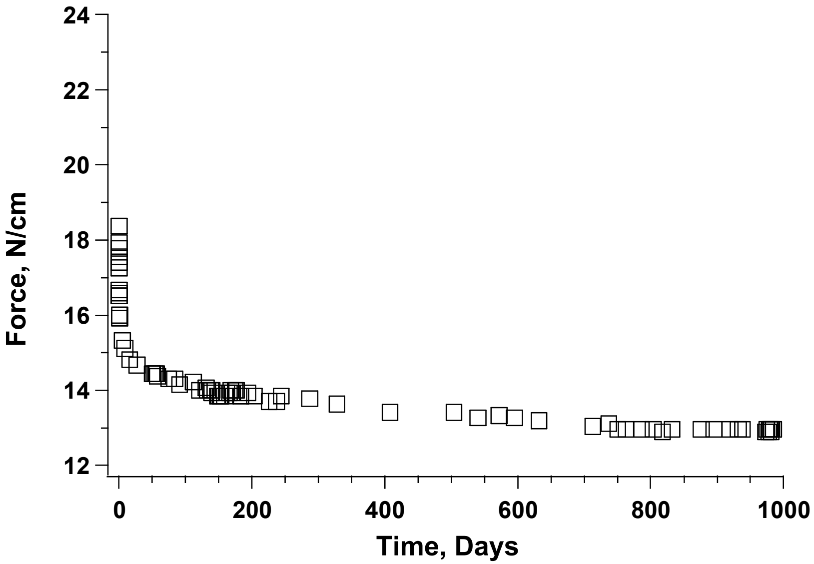


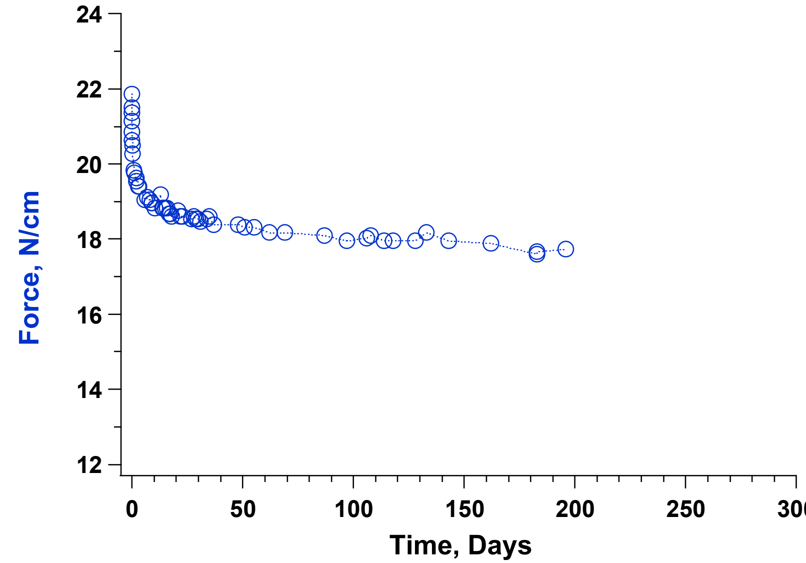
Over-compression as alternative to heating

Gillen, K. T.; Bernstein, R.; Wilson, M. H. *Polymer Degradation and Stability,* Predicting and Confirming the Lifetime of O-rings 2005, 87, 257-270.

Long Term Compression Versus Force -Fluorosilicone

Simple Compression



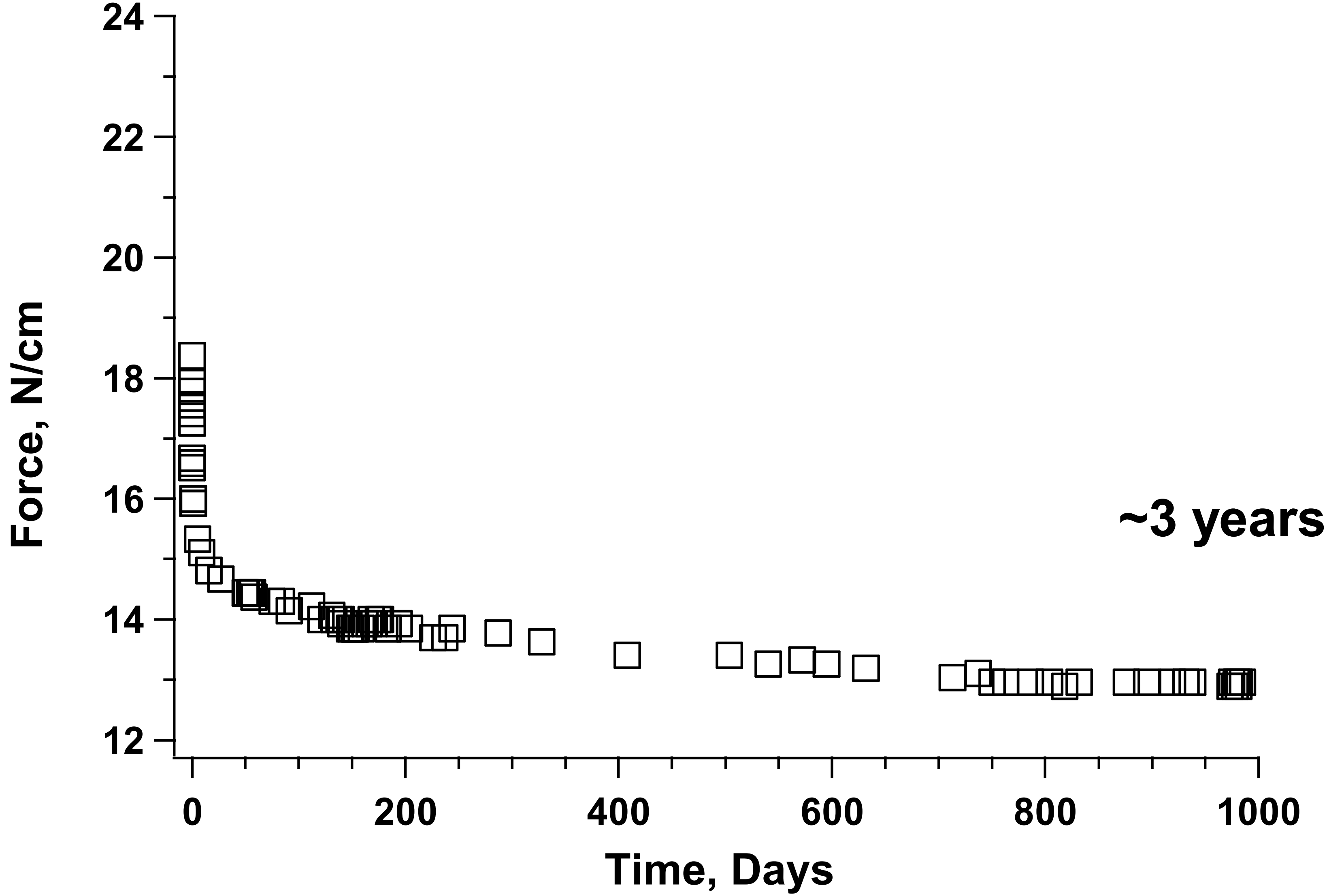


2.65 mm (104.25 mils) **2.5 mm (98.5 mils)**

Physical relaxation is a lengthy process

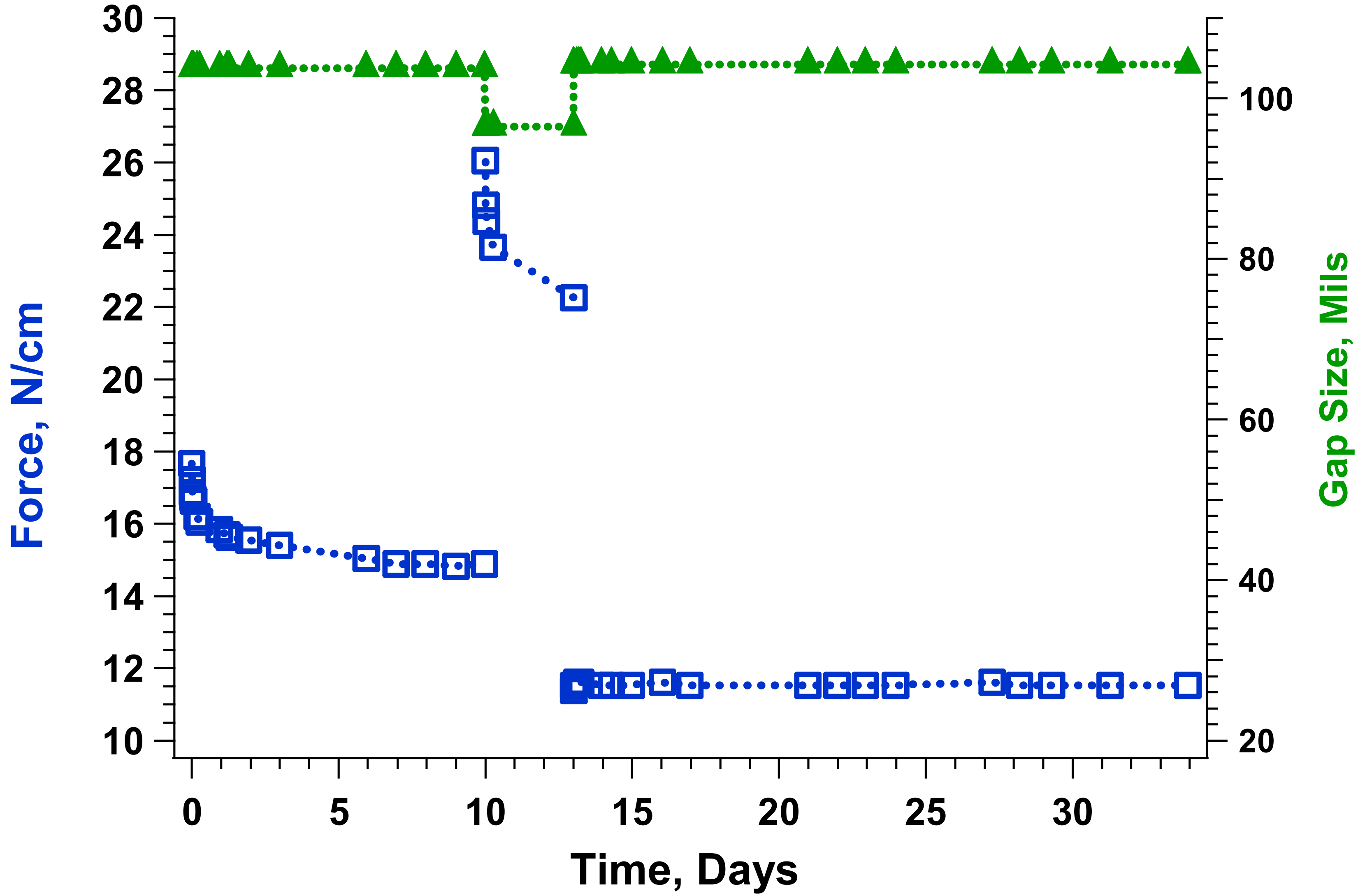
Bernstein, R.; Gillen, K. T. "*Fluorosilicone and Silicone O-Ring Aging Study*," SAND2007-6781, Sandia National Laboratories, 2007.
Bernstein, R.; Gillen, K. T. *Polymer Degradation and Stability, Predicting the Lifetime of Fluorosilicone O-rings 2009, 94, 2107-2133.*

Physical relaxation at RT



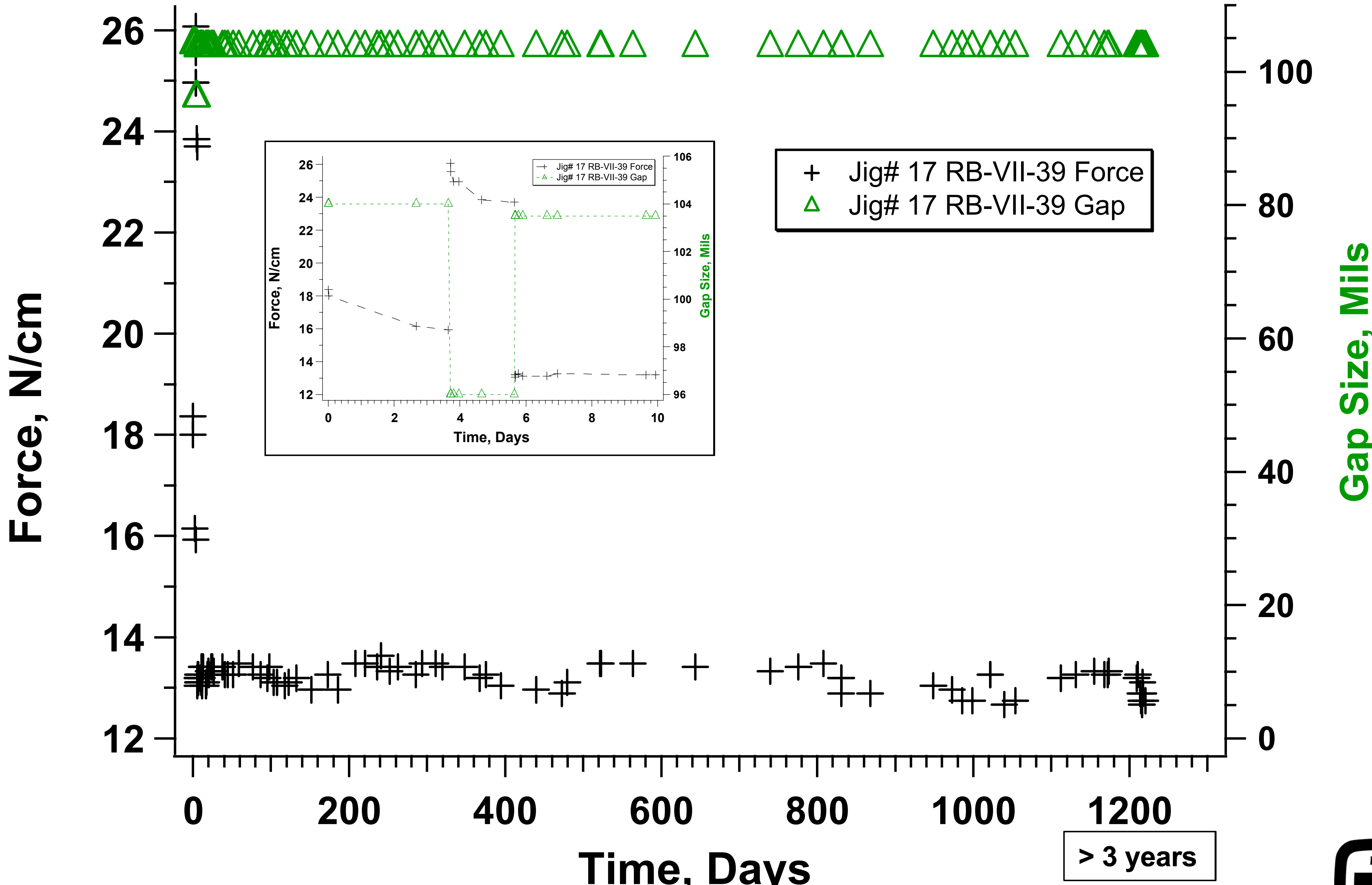
Bernstein, R.; Gillen, K. T. "*Fluorosilicone and Silicone O-Ring Aging Study*," SAND2007-6781, Sandia National Laboratories, 2007.
Bernstein, R.; Gillen, K. T. *Polymer Degradation and Stability, Predicting the Lifetime of Fluorosilicone O-rings 2009, 94, 2107-2133.*

Over Compression Methodology



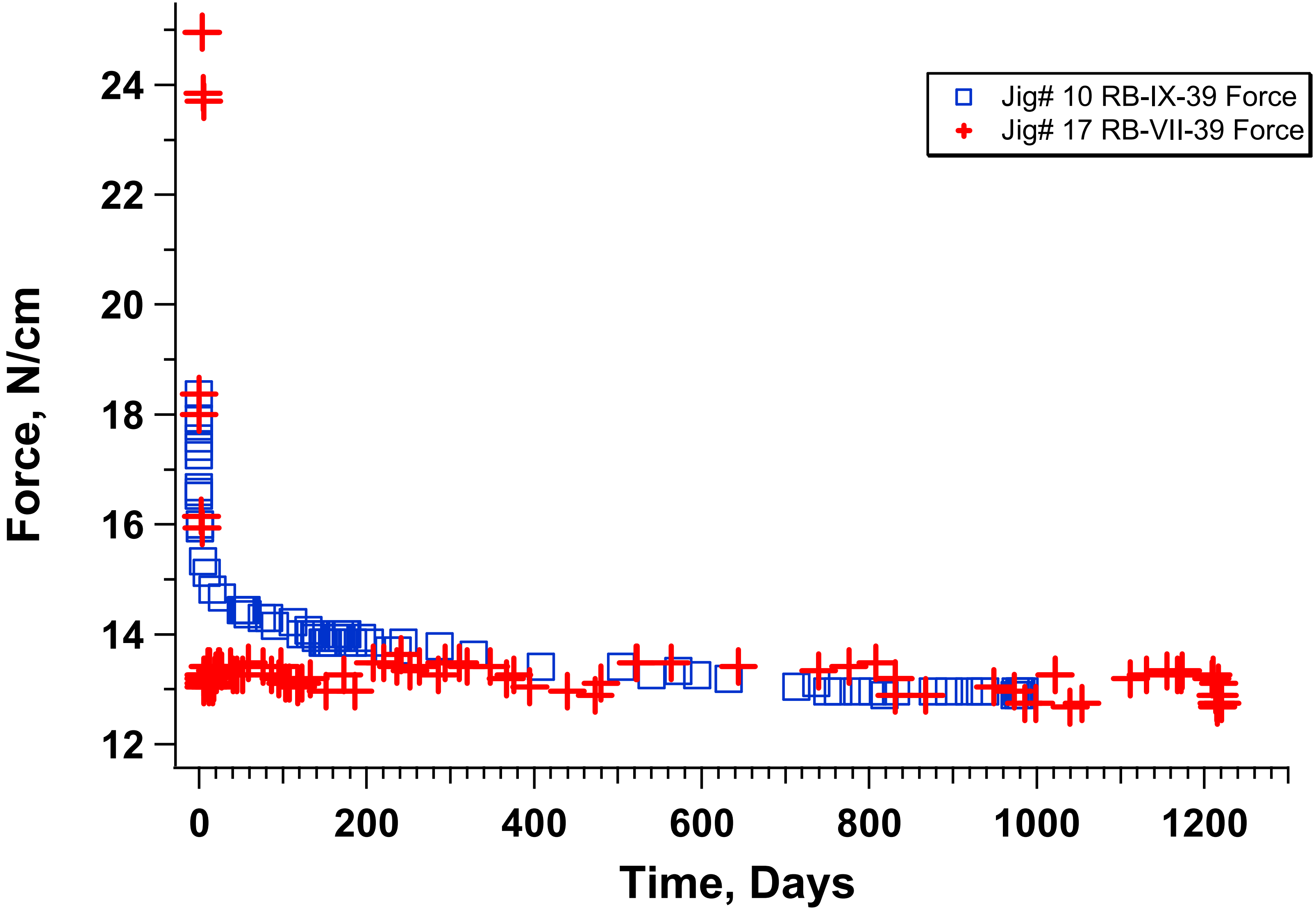
Bernstein, R.; Gillen, K. T. "*Fluorosilicone and Silicone O-Ring Aging Study*," SAND2007-6781, Sandia National Laboratories, 2007.
Bernstein, R.; Gillen, K. T. *Polymer Degradation and Stability, Predicting the Lifetime of Fluorosilicone O-rings 2009, 94, 2107-2133.*

Over compression



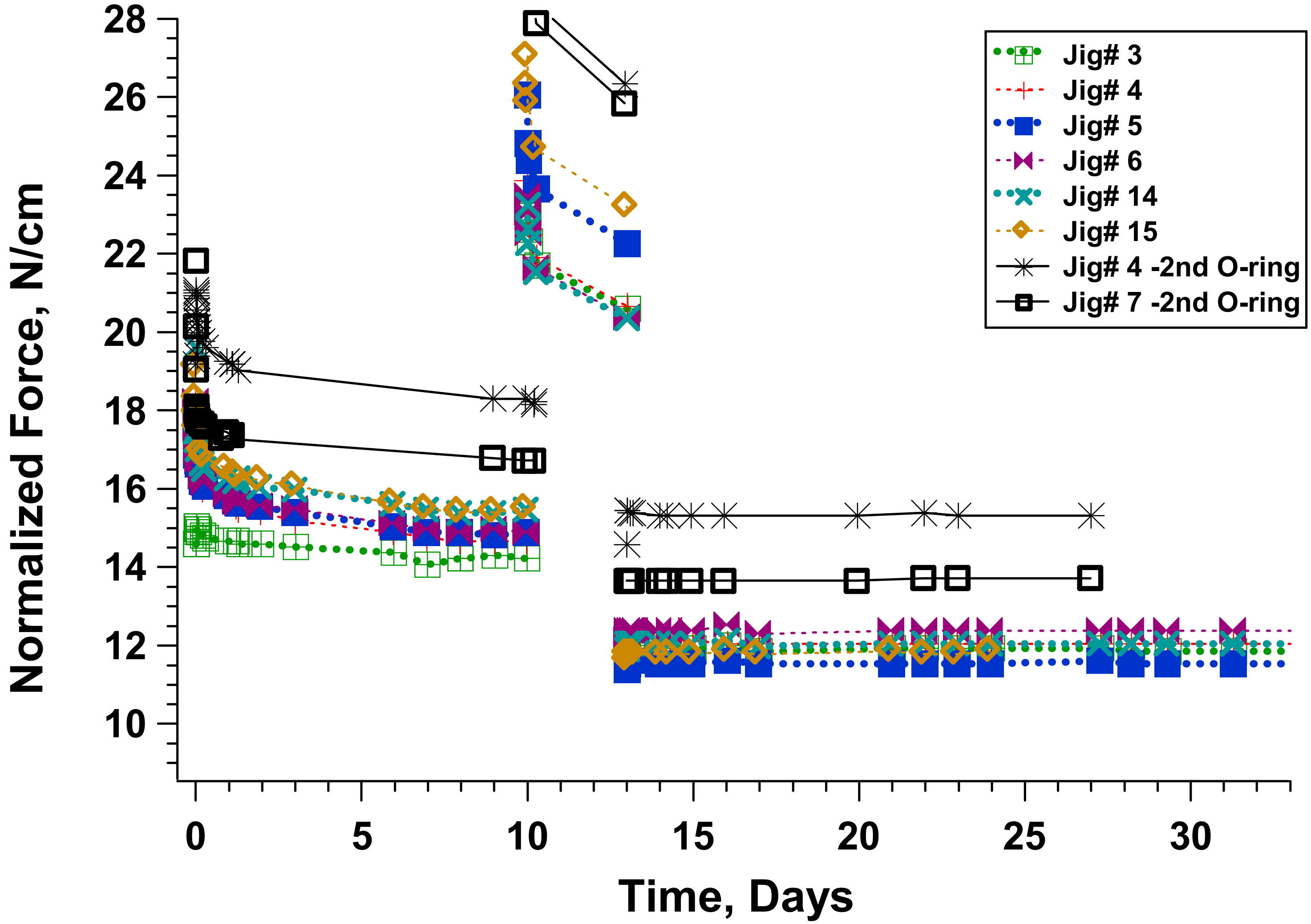
Bernstein, R.; Gillen, K. T. "*Fluorosilicone and Silicone O-Ring Aging Study*," SAND2007-6781, Sandia National Laboratories, 2007.
Bernstein, R.; Gillen, K. T. *Polymer Degradation and Stability, Predicting the Lifetime of Fluorosilicone O-rings 2009, 94, 2107-2133.*

Over compression comparison



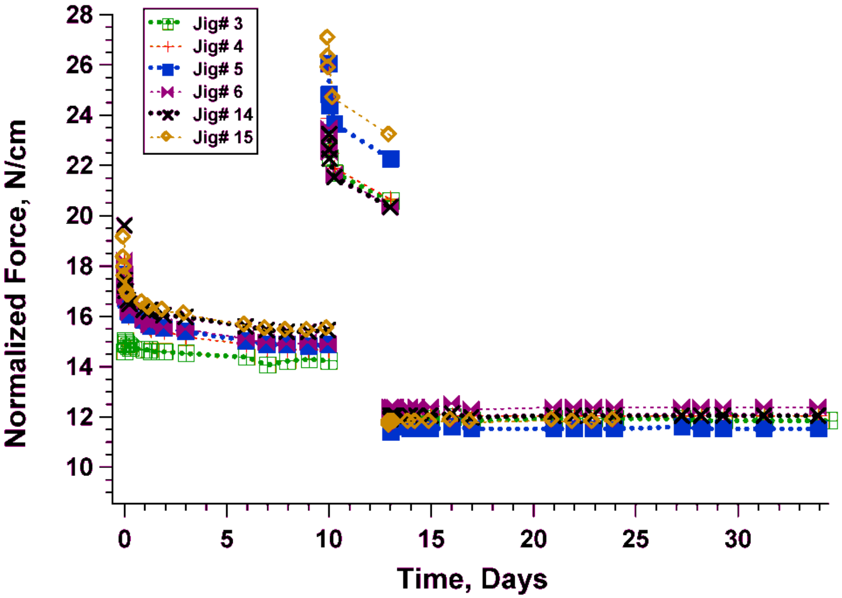
Bernstein, R.; Gillen, K. T. "*Fluorosilicone and Silicone O-Ring Aging Study*," SAND2007-6781, Sandia National Laboratories, 2007.
Bernstein, R.; Gillen, K. T. *Polymer Degradation and Stability, Predicting the Lifetime of Fluorosilicone O-rings 2009, 94, 2107-2133.*

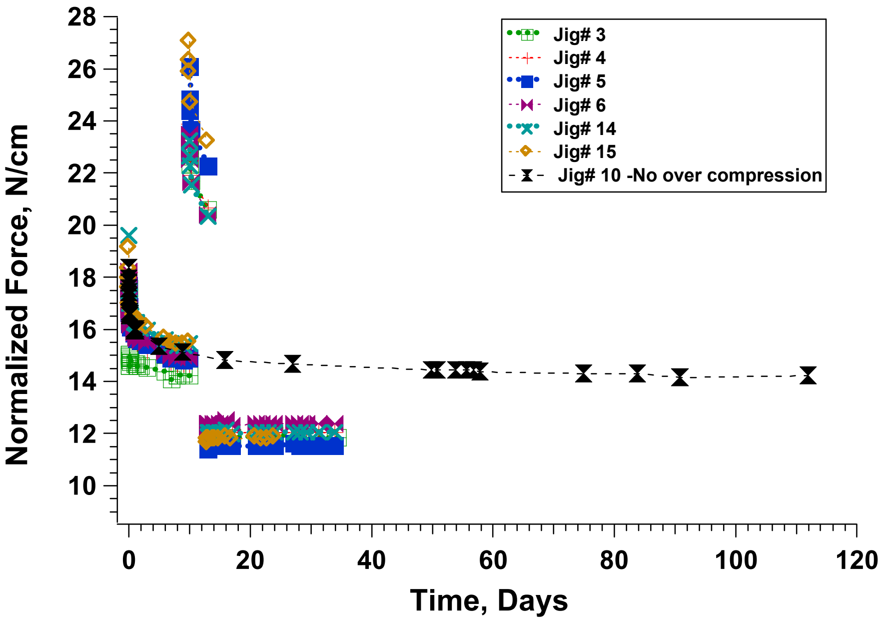
Over Compression: Multiple Jigs; Different O-rings



Bernstein, R.; Gillen, K. T. "*Fluorosilicone and Silicone O-Ring Aging Study*," SAND2007-6781, Sandia National Laboratories, 2007.
Bernstein, R.; Gillen, K. T. *Polymer Degradation and Stability, Predicting the Lifetime of Fluorosilicone O-rings 2009, 94, 2107-2133.*

Over Compression: Multiple Jigs; Same O-ring





Good reproducibility **Much shorter equilibrium time**

Bernstein, R.; Gillen, K. T. "*Fluorosilicone and Silicone O-Ring Aging Study*," SAND2007-6781, Sandia National Laboratories, 2007.
Bernstein, R.; Gillen, K. T. *Polymer Degradation and Stability, Predicting the Lifetime of Fluorosilicone O-rings 2009, 94, 2107-2133.*

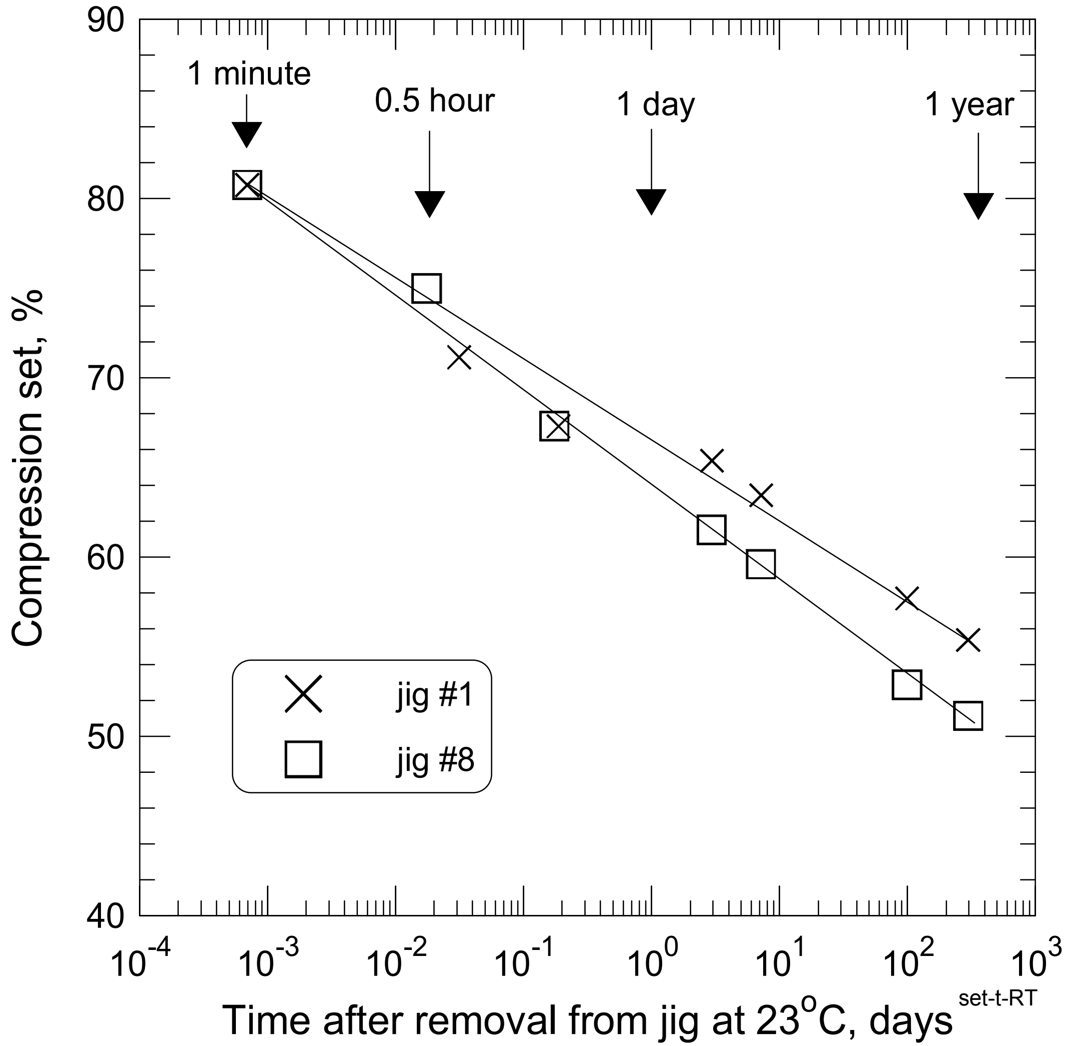
Over Compression: Multiple Jigs; Different O-rings

Jig#	~10 day	~After over compression	~ % drop
3	14.2	11.9	16
4	14.67	12.04	18
5	14.89	11.53	23
6	14.89	12.37	17
14	15.4	12.05	22
15	15.4	11.78	24
4	18.3	15.3	16
7	16.7	13.7	18

Bernstein, R.; Gillen, K. T. "*Fluorosilicone and Silicone O-Ring Aging Study*," SAND2007-6781, Sandia National Laboratories, 2007.
Bernstein, R.; Gillen, K. T. *Polymer Degradation and Stability, Predicting the Lifetime of Fluorosilicone O-rings 2009, 94, 2107-2133.*

O-ring Compression Set

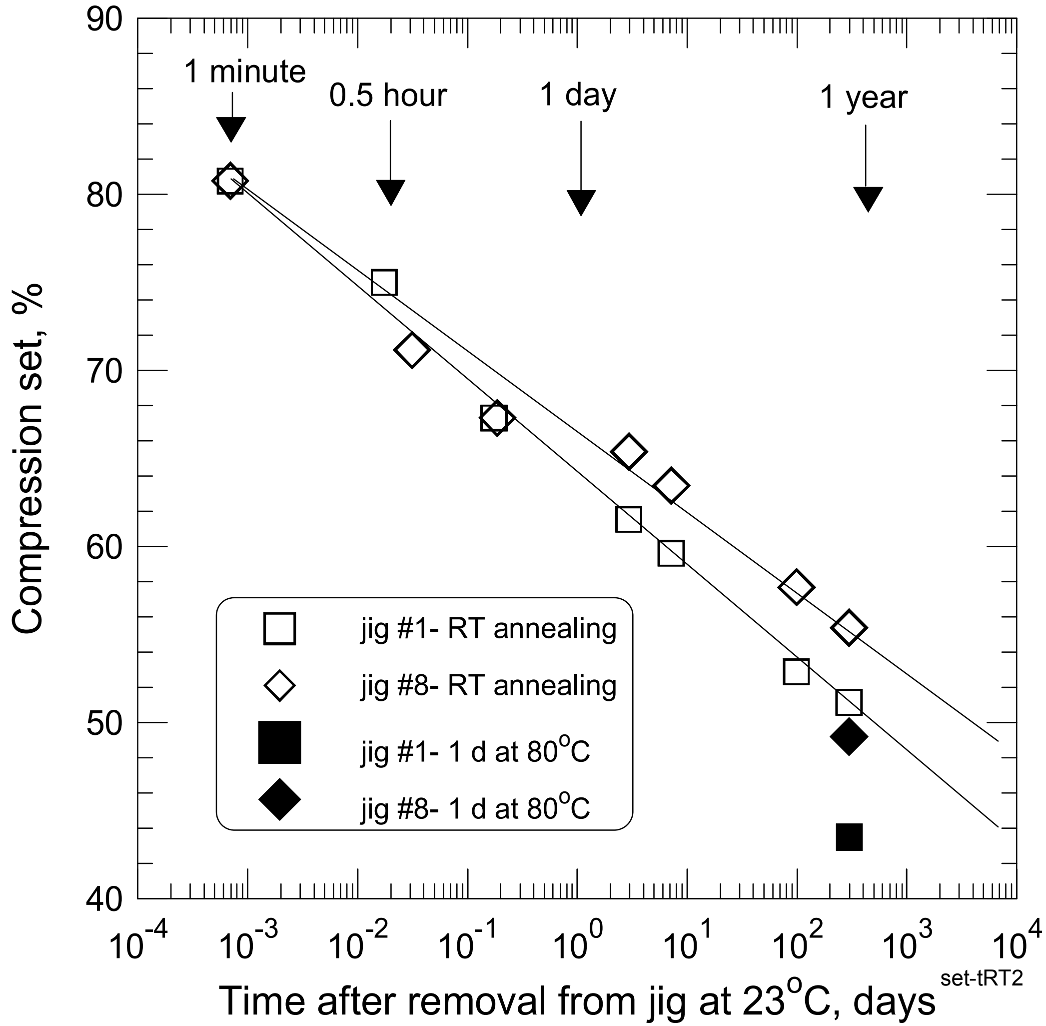
Compression set easy to measure but *changing* with time



Equilibrium set can take a long time

Gillen, K. T.; Bernstein, R.; Wilson, M. H. *Polymer Degradation and Stability,* Predicting and Confirming the Lifetime of O-rings 2005, 87, 257-270.

Compression set

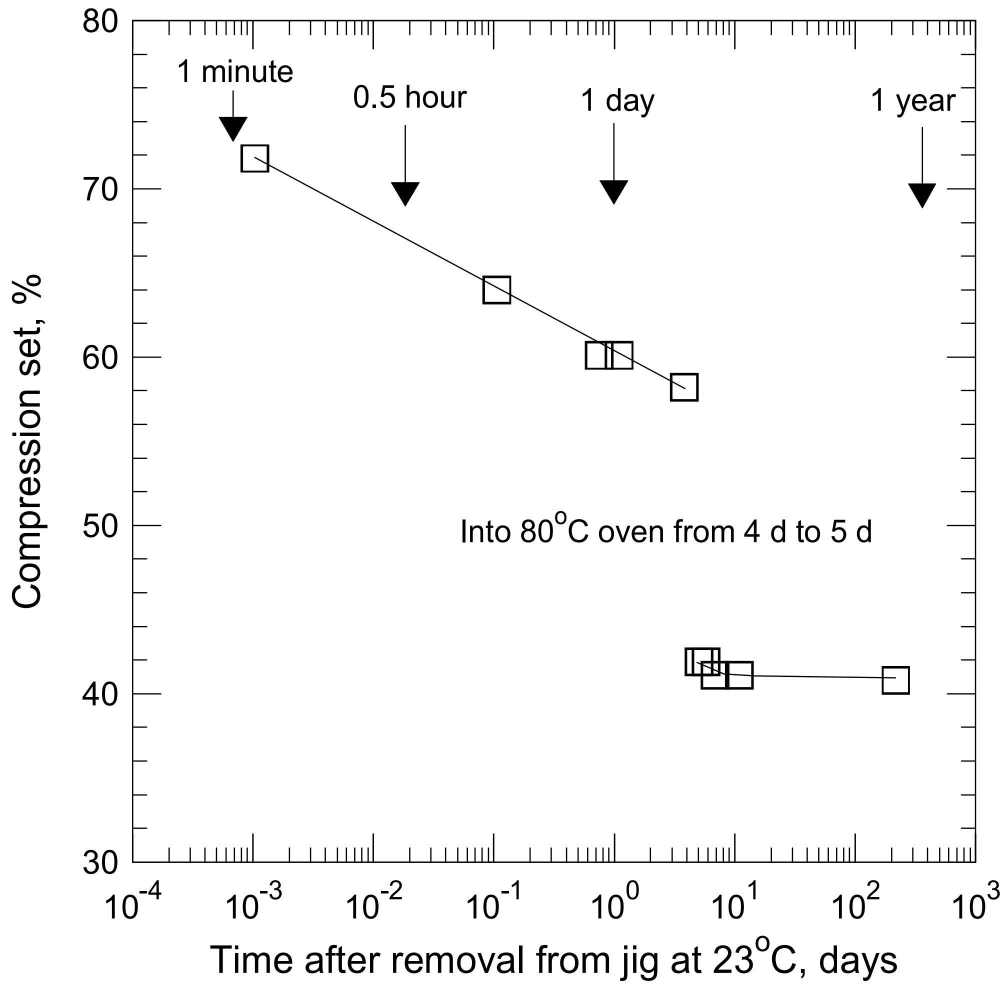


After ~1 year at RT, samples put into 80 C oven for ~ 1 day

(would have taken ~30 years at RT to continue that drop)

Gillen, K. T.; Bernstein, R.; Wilson, M. H. *Polymer Degradation and Stability,* Predicting and Confirming the Lifetime of O-rings 2005, 87, 257-270.

Equilibrium Compression Set



After oven exposure; additional 210 days at room temperature only dropped the set by another 1%

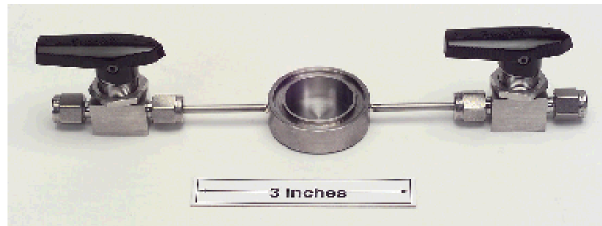
Gillen, K. T.; Bernstein, R.; Wilson, M. H. *Polymer Degradation and Stability,* Predicting and Confirming the Lifetime of O-rings 2005, 87, 257-270.

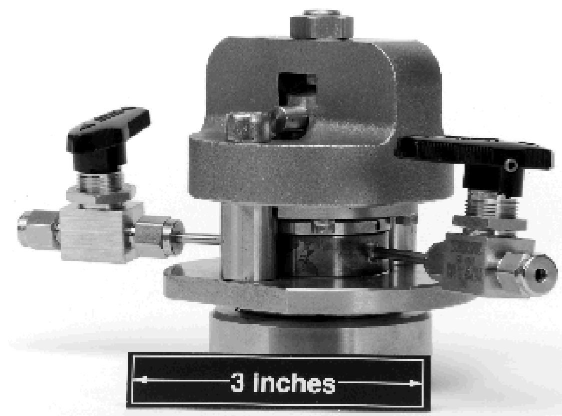
What is ‘Lifetime’ for an O-ring?

(Our) O-ring Job description: Keep out water and air

Measure leak rate; use that to define ‘death’

Mark Wilson's Jig

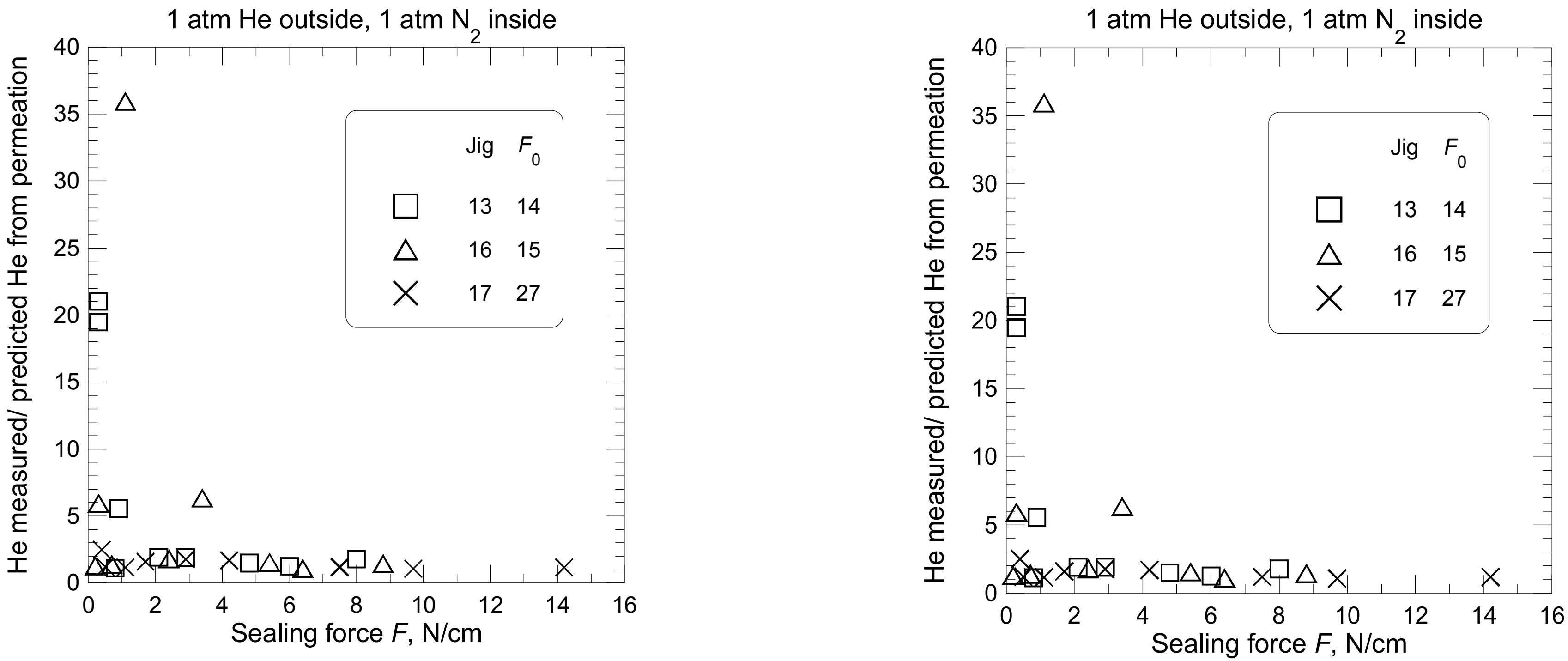




Helium leak detector

Gillen, K. T.; Bernstein, R.; Wilson, M. H. *Polymer Degradation and Stability,* Predicting and Confirming the Lifetime of O-rings 2005, 87, 257-270.

Leak Testing of O-rings



1.78 mm cross section **2.62 mm cross section**

Death ≈ 1 N/cm sealing force

Gillen, K. T.; Bernstein, R.; Wilson, M. H. *Polymer Degradation and Stability,* Predicting and Confirming the Lifetime of O-rings 2005, 87, 257-270.