SAND2005-7752C

Pacifichem 2005

Honolulu, Hawaii, December 19, 2005

Recent Results Indicative of Non-Arrhenius Behavior

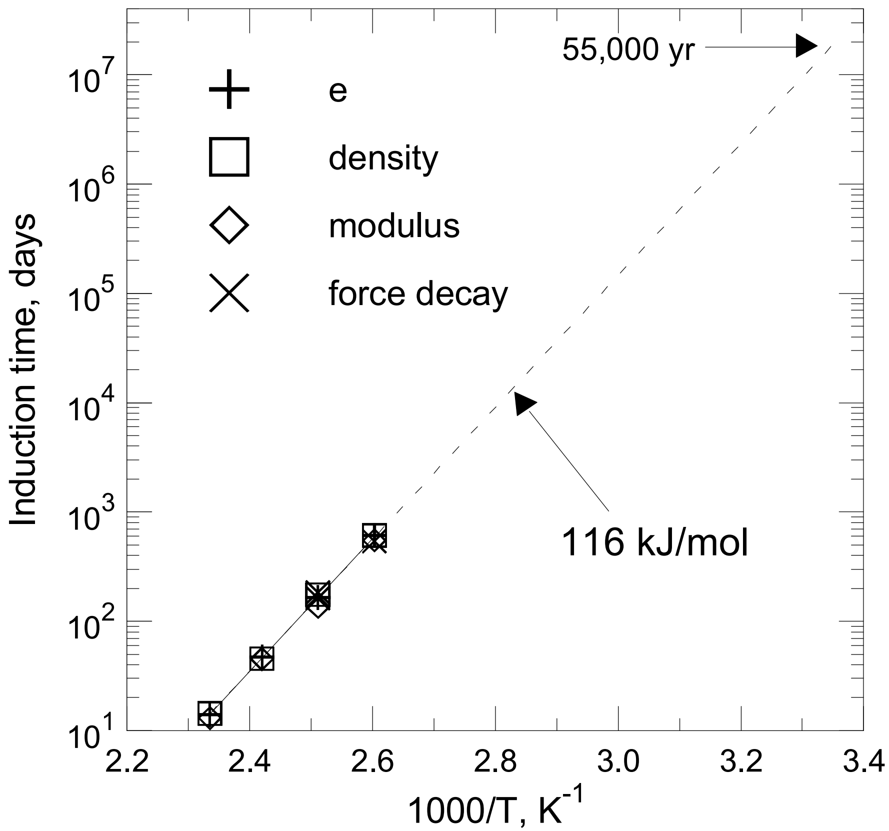
Kenneth T. Gillen[1], Matthew Celina[2] and Robert Bernstein
Organic Materials Department, Box 5800, MS-1411
Sandia National Laboratories, Albuquerque, NM 87185-1411

[1] Consultant
[2] Contractor

Sandia is a multiprogram laboratory operated by Sandia Corporation, a Lockheed Martin Company, for the United States Department of Energy's National Nuclear Security Administration under contract DE-AC04-94AL85000.

Historic Arrhenius Approach for Lifetime Prediction

- Measure "failure" times & create Arrhenius plot [$t \sim \exp(-E_a/RT)$]
- Extrapolate to make predictions
- Typical data over a factor of 20- anything looks "Arrhenius"

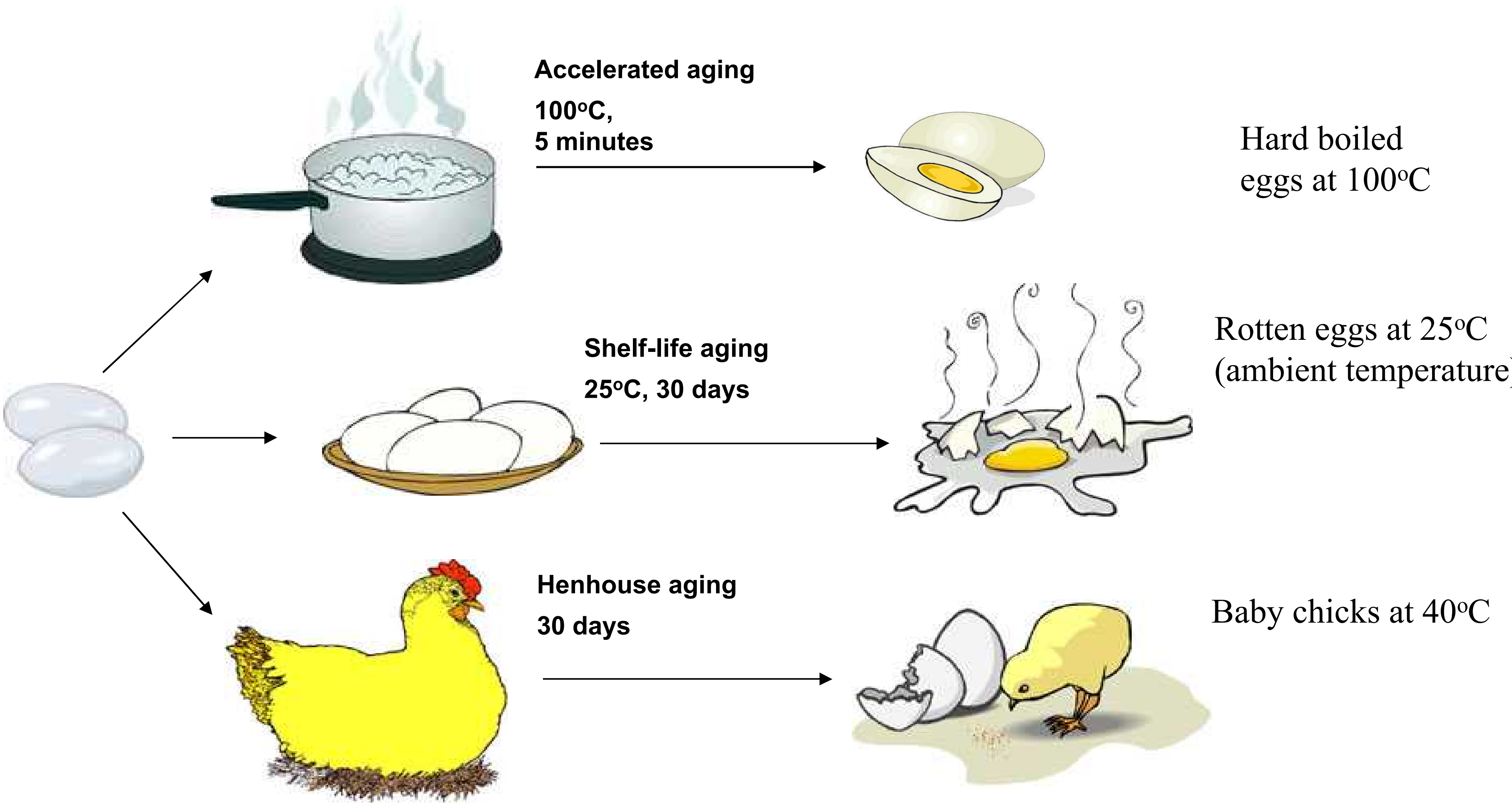


EPDM O-RING

- Long life predicted if E_a remains constant
- But long extrapolation (extrapolation range ~2 data range)
- Therefore little confidence in the prediction

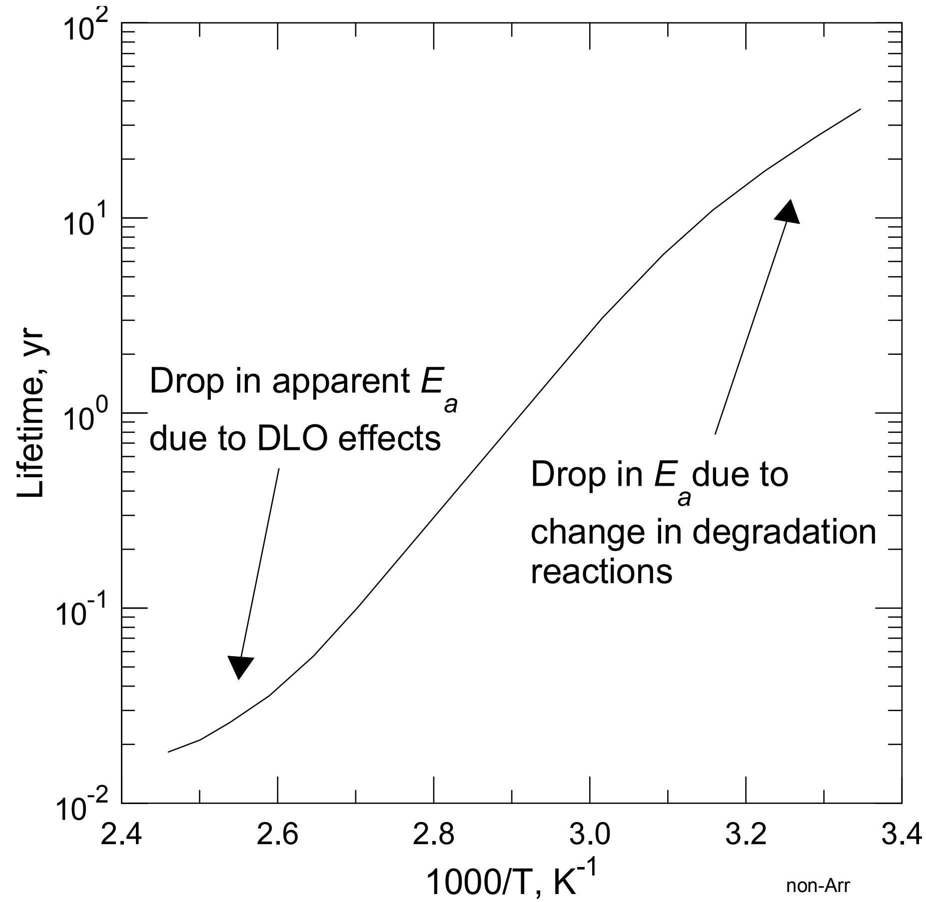
Reference- Gillen, Celina, Clough and Wise, Review paper in **Trends in Polymer Science,** 5, 250 (1997).

Concern- relative mix of reactions may change as temperature increased



Selected Phenomena That May Result in Non-Arrhenius Behavior

- Dominant reactions can change with T
  -tends to give **<u>lower</u>** E_a **<u>as T lowered</u>**)
- Polymer transition region (T_g or T_{mp}).
- Reactions can depend on sample geometry
  -diffusion-limited oxidation (DLO)
  -tends to give **<u>lower</u>** E_a **<u>as T raised</u>**)

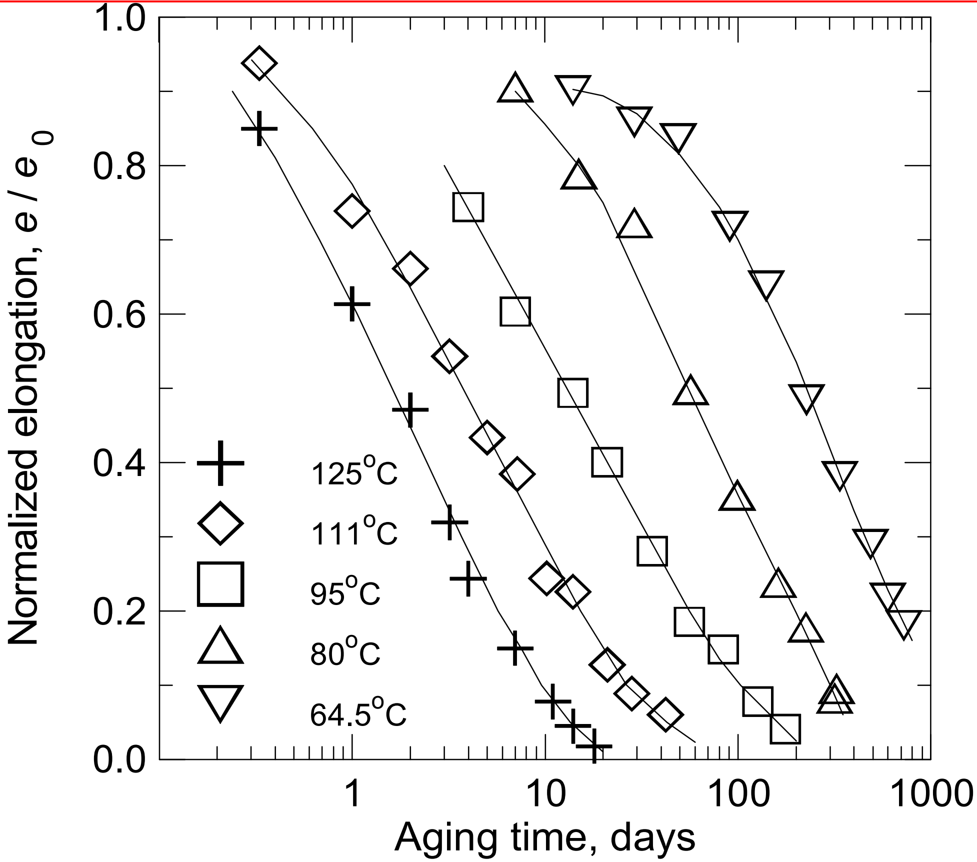


Other standard Arrhenius approach problems

1. Most data eliminated. Solution- **<u>time-temperature superposition</u>**.
2. No confirmation of E_a extrapolation. Solution- **<u>ultrasensitive O_2 consumption</u>** measurements extending into extrapolation region.

Improved approach- time-temperature superposition

Principle of accelerated aging- raise *T* to increase overall reaction rate
- **implies curves at 2 *T*'s related by constant multiplier (constant acceleration)**
- **implies same curve shape when plotted versus log time**
- **choose reference *T* (multiplicative shift factor $a_T = 1$)**
- **at each *T*, find empirical a_T that gives optimum superposition**



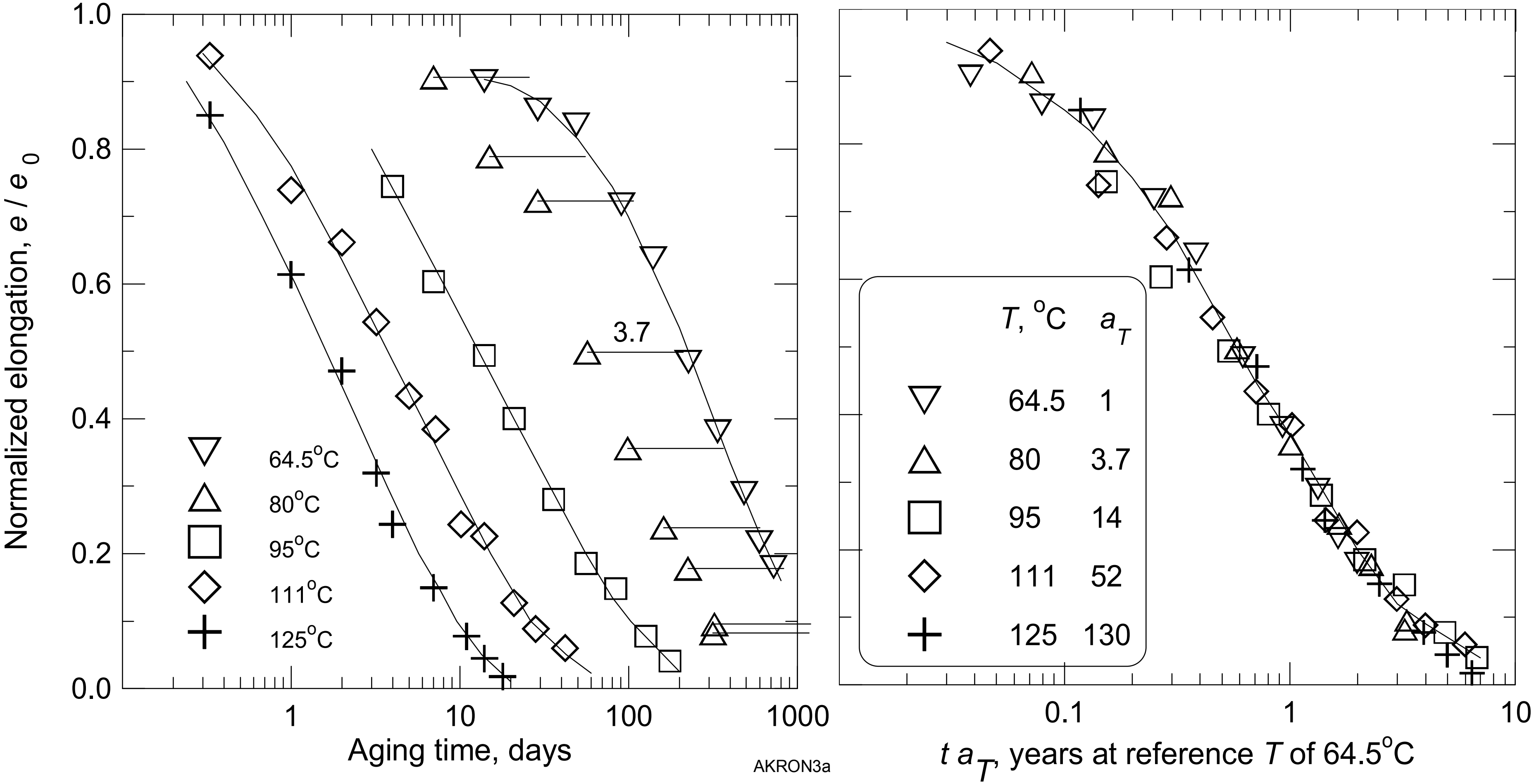
Commercial nitrile rubber
- *e* vs. *T* and time

NOTE
- **2 years of aging at 64.5°C**
- **data covers a factor of ~130**
- **this gives better Arrhenius test**
- **this also minimizes extrapolation**

Ref.- J. Wise, K. T. Gillen and R. L. Clough, Polym. Degrad. & Stabil., 49, 403 (1995).

Nitrile- empirical *t-T* superposition at 64.5°C

a_T defined as shift factor for temperature T



Normal Arrhenius- 1 point per T (e.g., time to $e/e_0 = 0.25$)
Superposition- every datum point is used in the analysis

Sandia National Laboratories

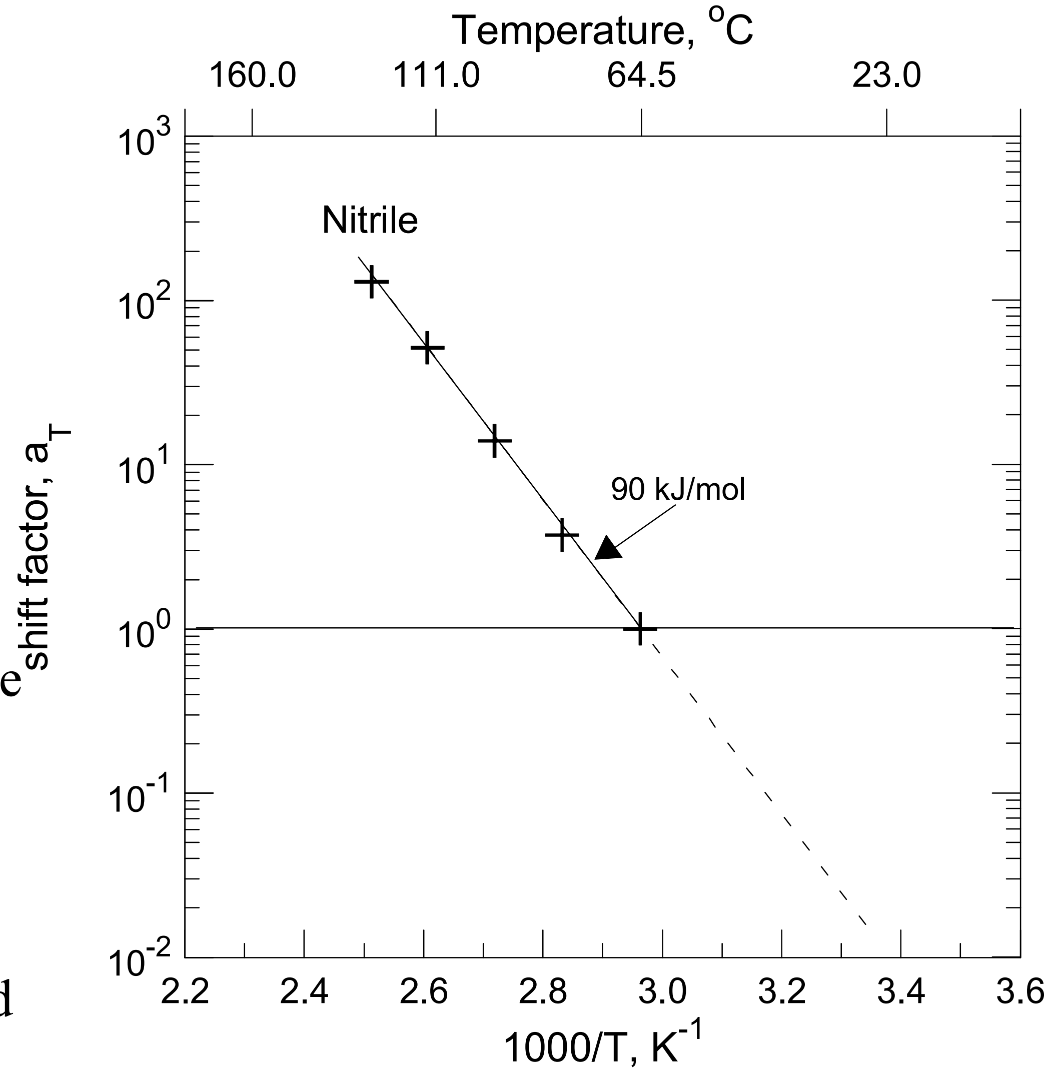
Can Test Various Models on Empirical a_T's

If Arrhenius,

$$a_T = \exp\frac{E_a}{R}\left(\frac{1}{T_{ref}} - \frac{1}{T}\right)$$

Dashed line ($a_T < 1$) gives <u>unconfirmed</u> extrapolation to lower T's

- need access to low temperature regime
- implies need for ultrasensitive analytical technique
- property must be correlated to aging mechanism
- since oxidation dominates air-exposed samples, solution is **O_2 consumption measurements**

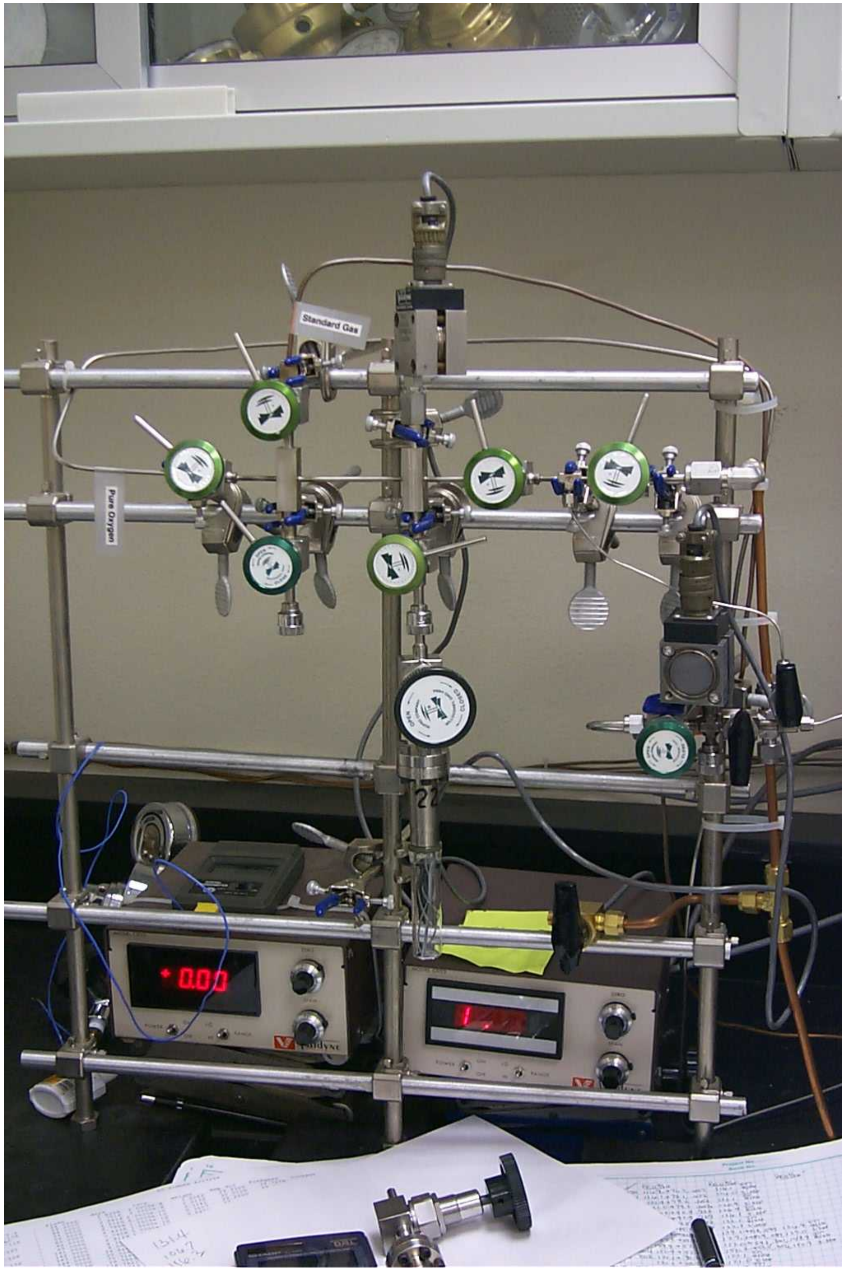


Ref.- J. Wise, K. T. Gillen and R. L. Clough, Polym. Degrad. & Stabil., <u>49</u>, 403 (1995).

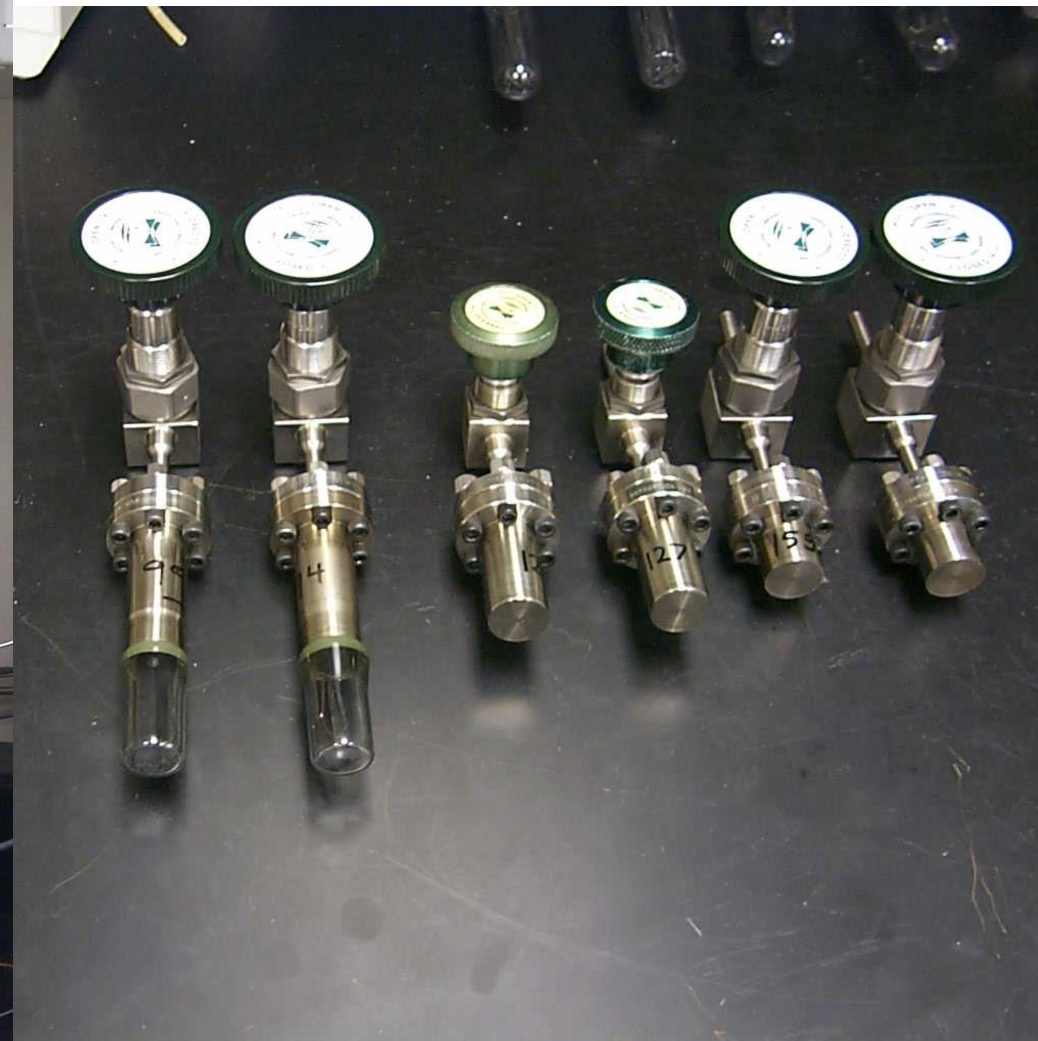
Sandia National Laboratories

Ultrasensitive Oxygen Consumption (UOC)

Gas handling line

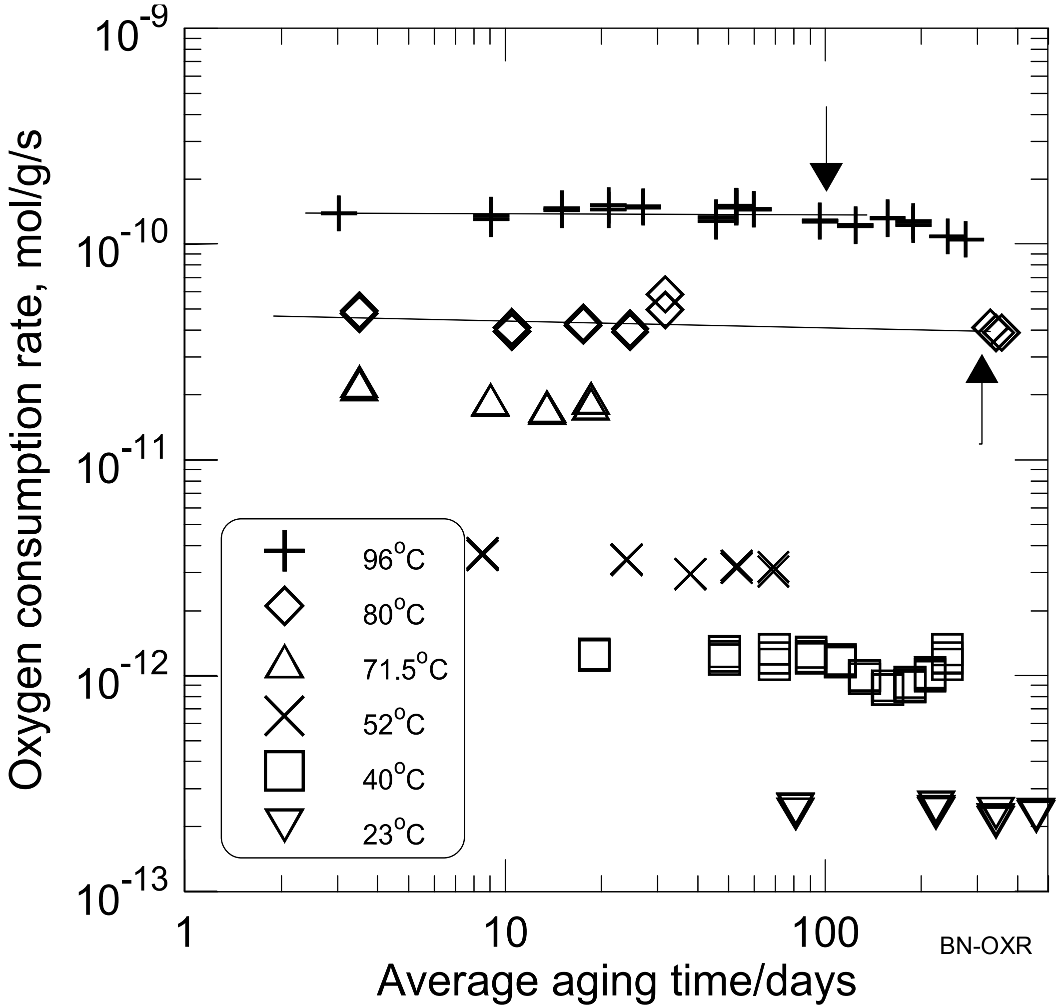


Typical sample containers



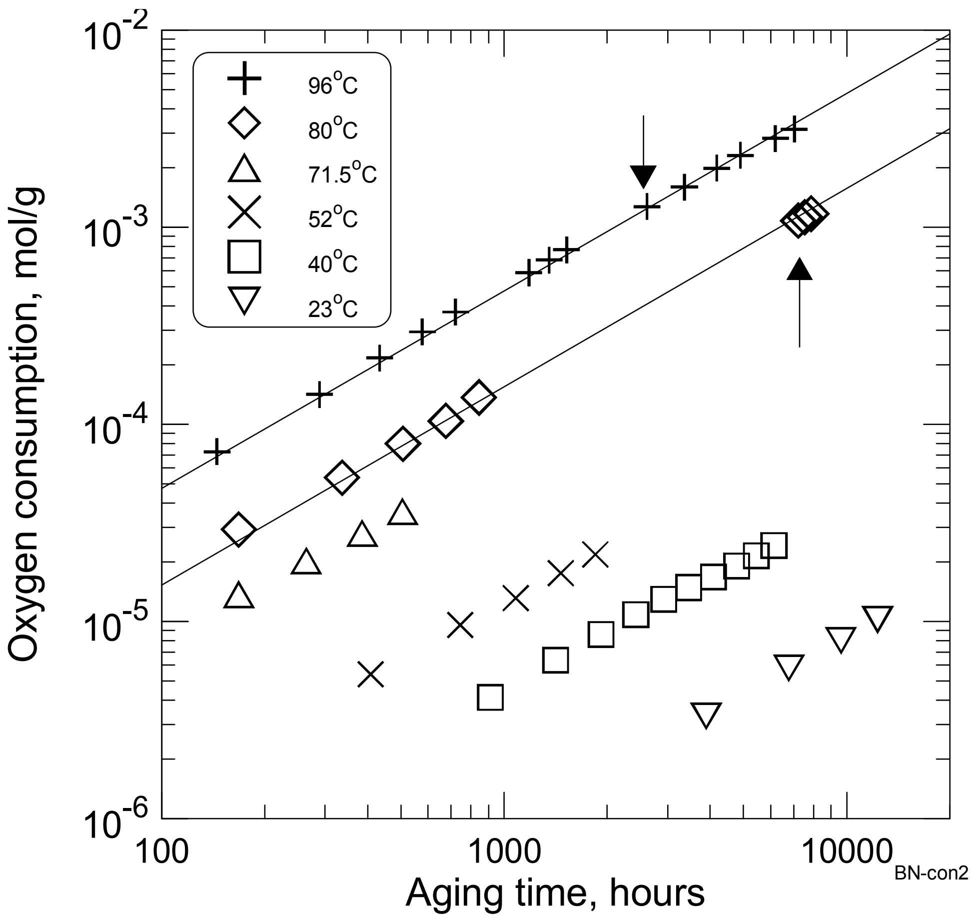
Sandia National Laboratories

O_2 consumption results for nitrile rubber

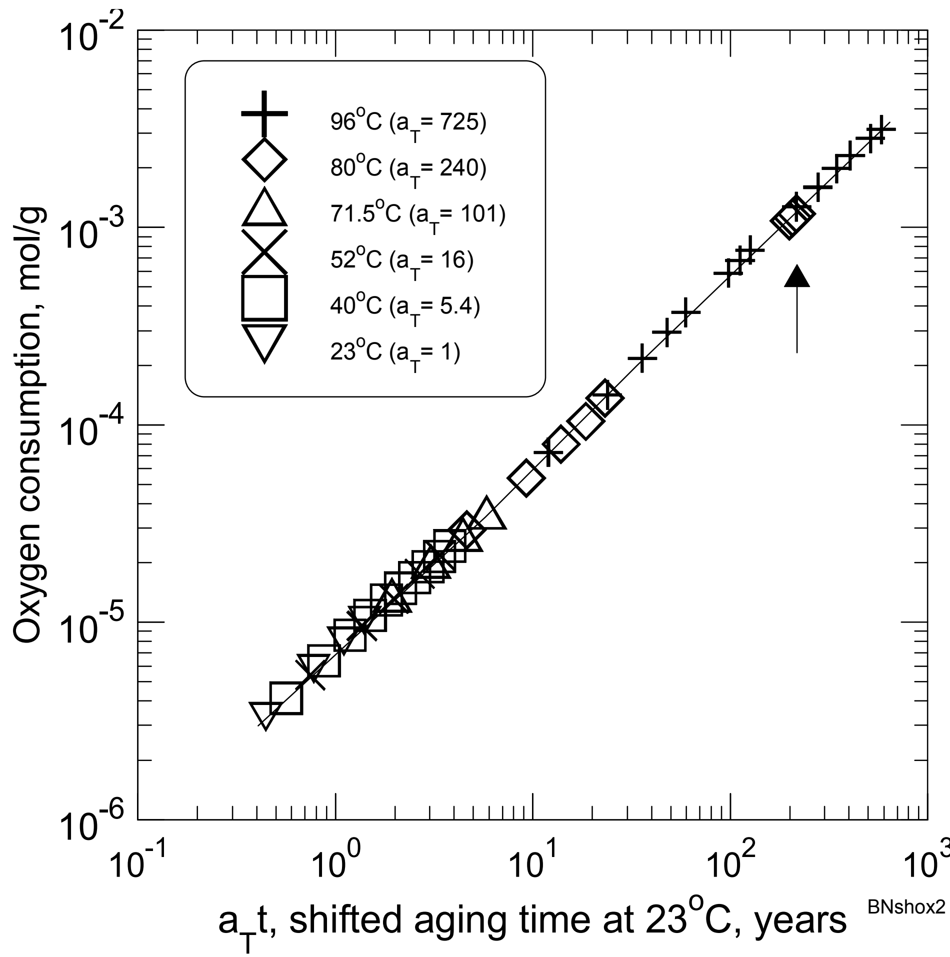


- elongation taken down to 65°C (2 years of aging)
- UOC results obtained down to room *T* (23°C)
- constant rate at each *T*
- consistent with constant acceleration assumption
- arrows denote time to 10% of initial elongation

Integrated O_2 consumption

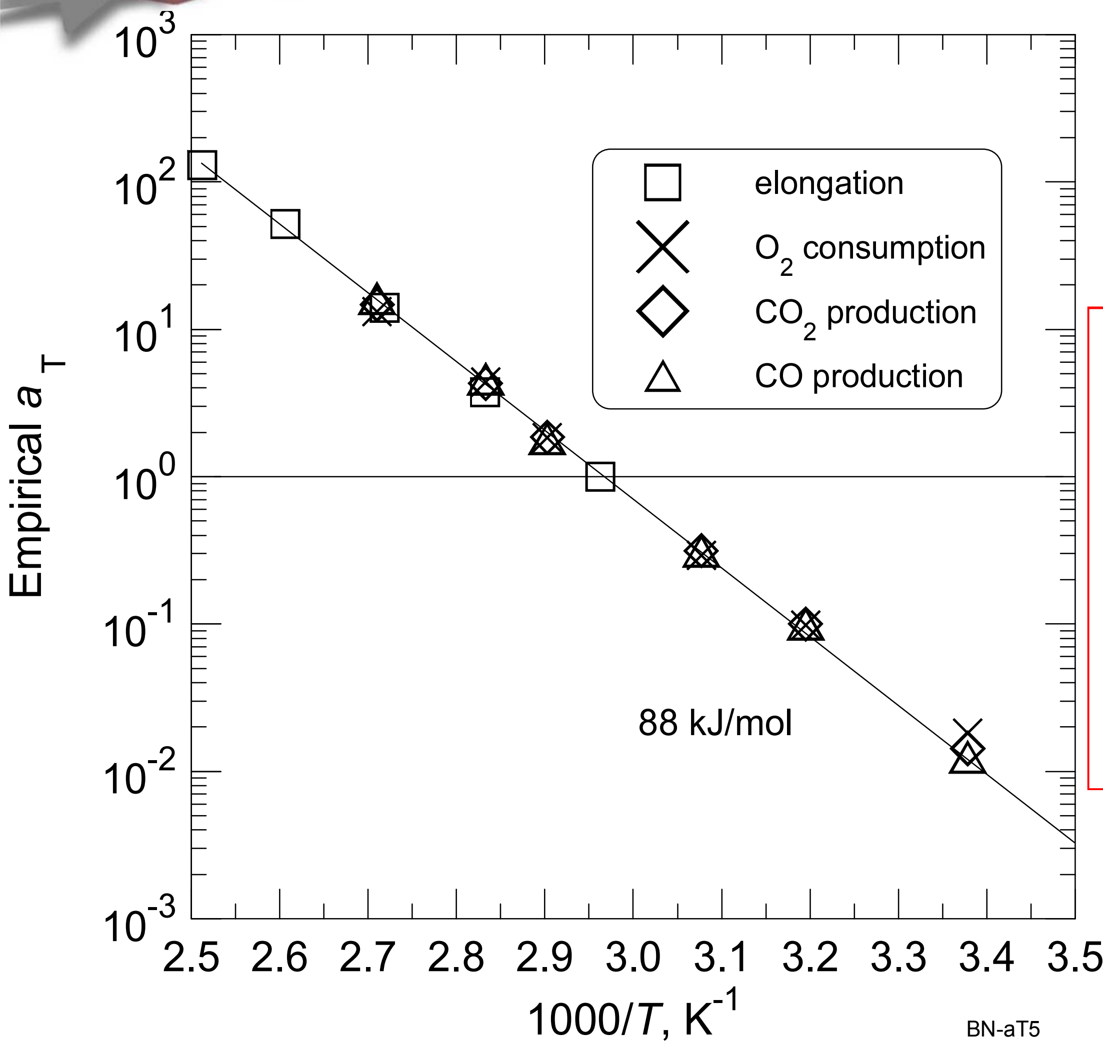


t-T superposition of integrated consumption



Sandia National Laboratories

Compare shift factors of elongation and UOC



Arrhenius behavior confirmed for nitrile rubber material

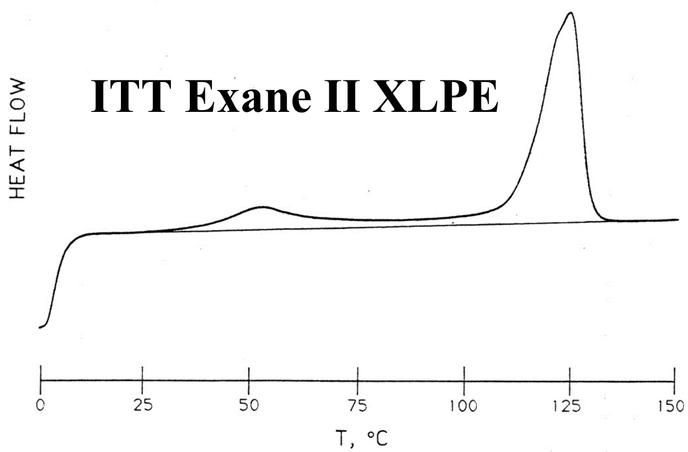
Note: CO_2 and CO production rates have same E_a as O_2 consumption

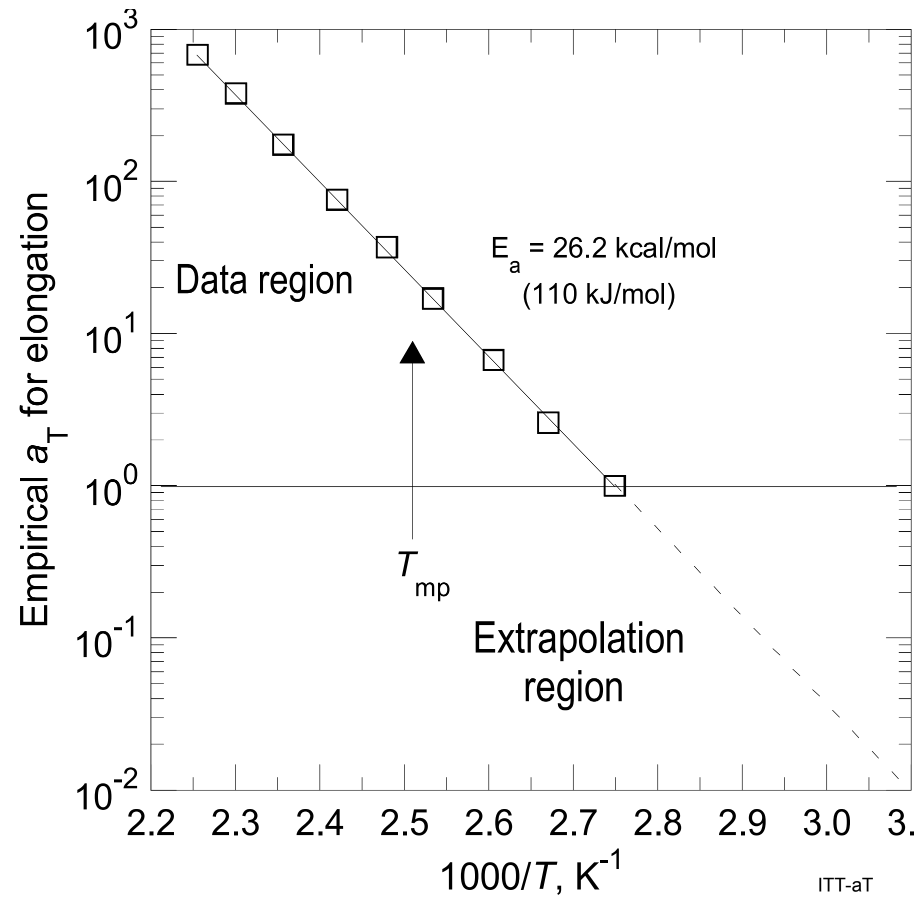
- Same E_a in overlap region confirming connection of UOC & elongation
- UOC finds same E_a below 65°C confirming Arrhenius extrapolation assumption

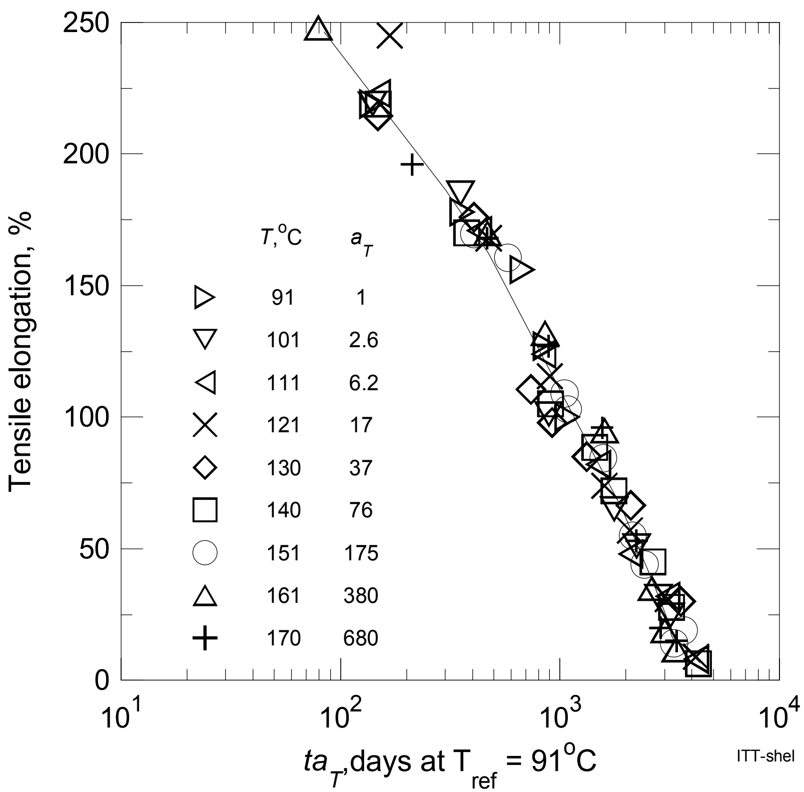
Sandia National Laboratories

Elongation- semi-crystalline material through T_{mp}

(Reference- Gillen, Assink & Bernstein- SAND Report 2005-7331)







Find excellent superposition for data above and below main melting region

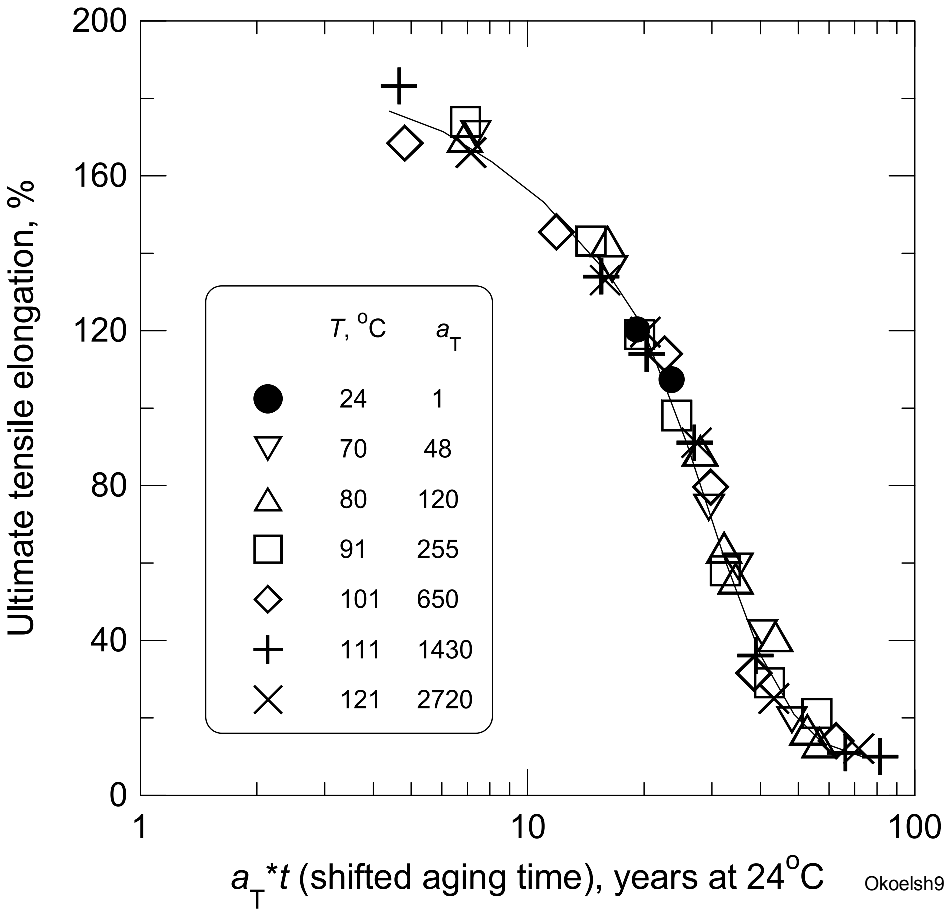
Find constant Arrhenius slope through transition region

Sandia National Laboratories

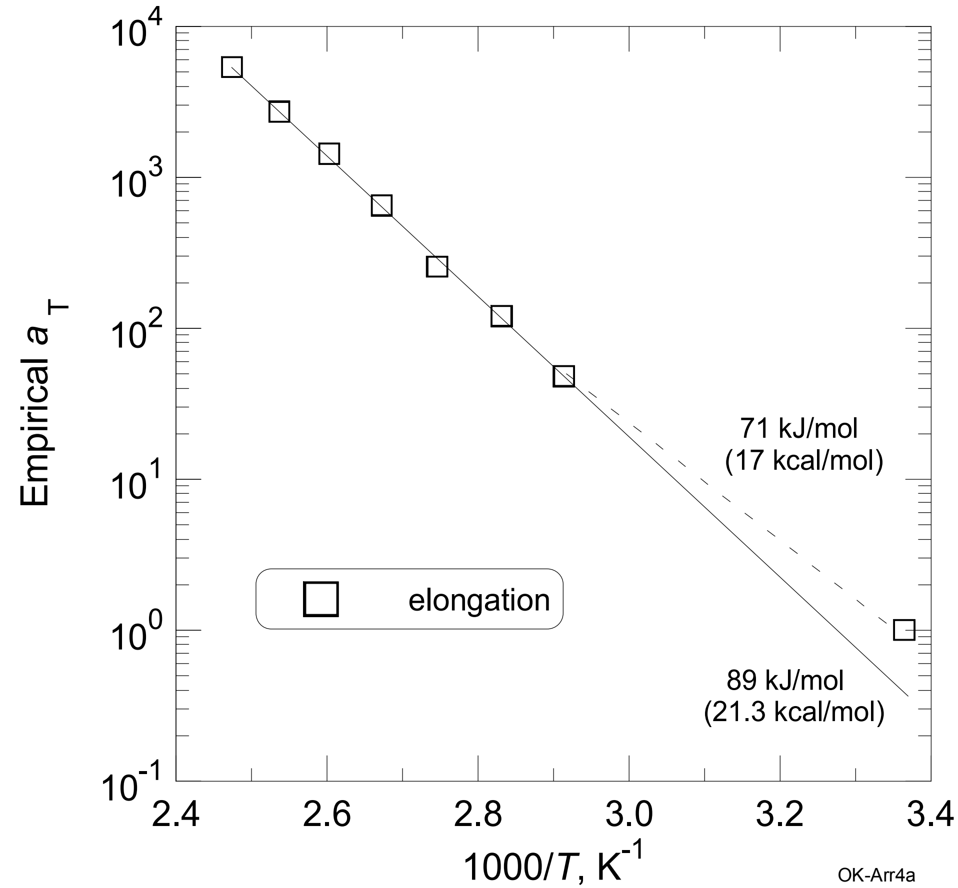
Non-Arrhenius evidence for chloroprene materials

Have 19-23 year data at 24 °C for Okonite neoprene

t-T **superposition with 24°C reference *T***



Non-Arrhenius **elongation results**



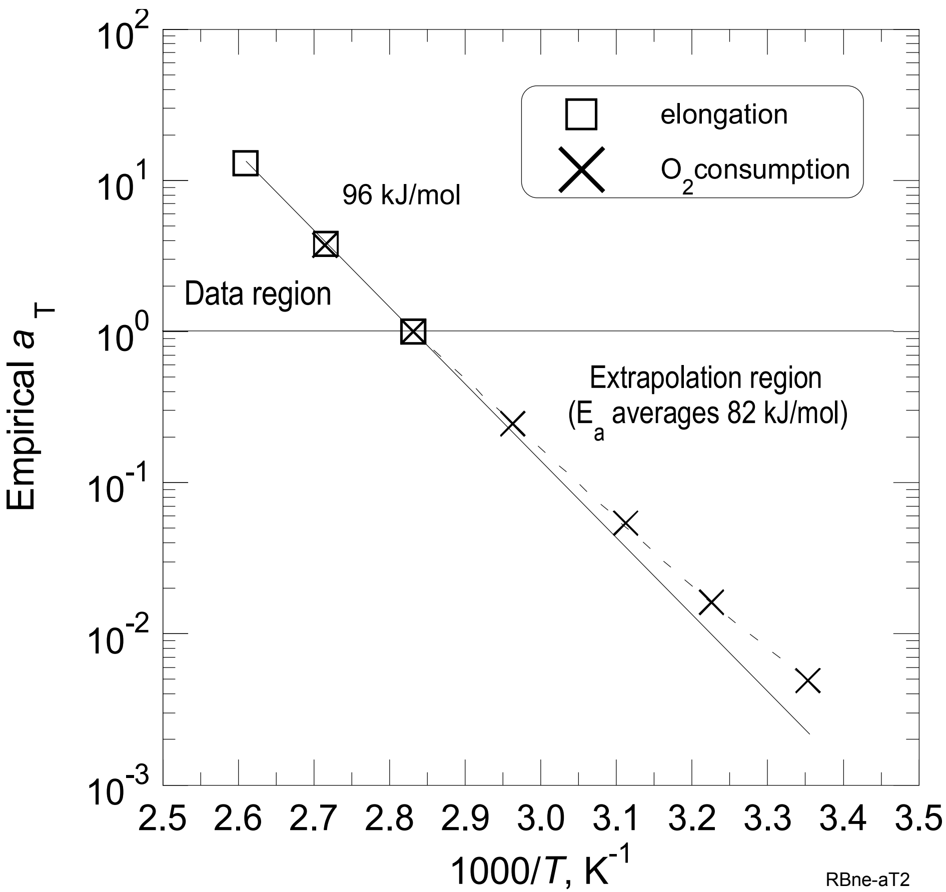
Note- room temperature lifetime reduced by ~60%

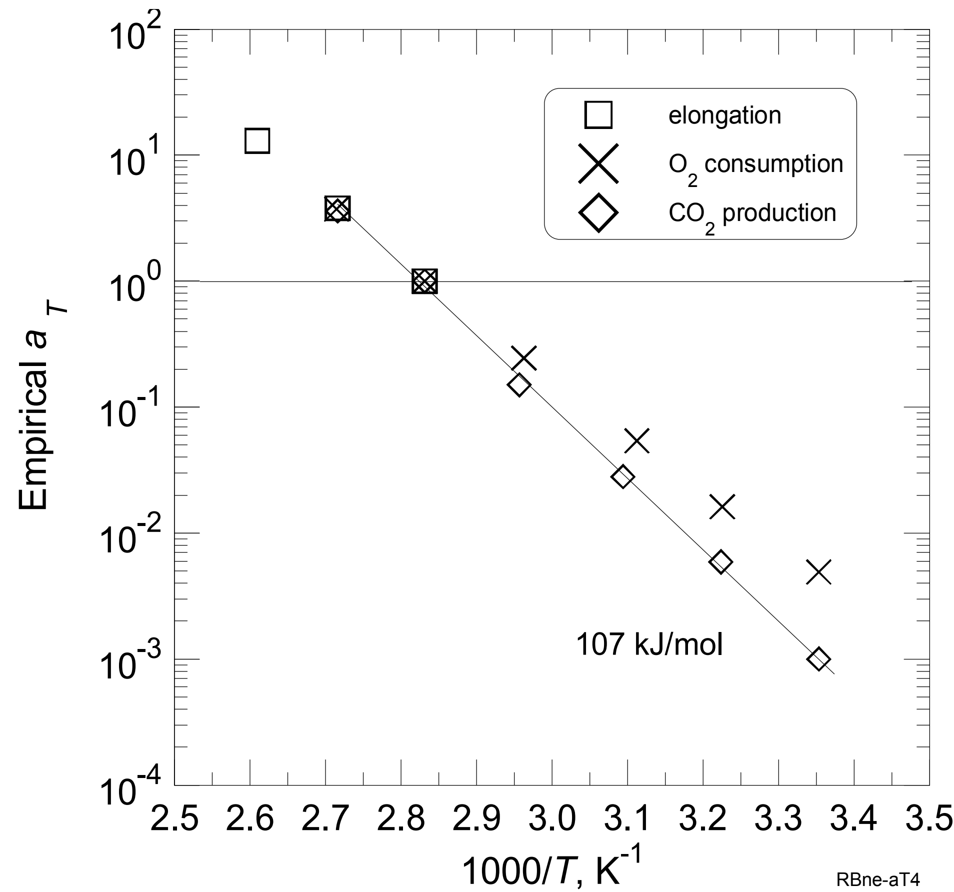
Ref.- Gillen, Bernstein and Derzon Polymer Degradation and Stability, 87, 57 (2005).

Non-Arrhenius for O_2 consumption of 2nd neoprene

Rockbestos neoprene cable jacket- evidence from UOC results

CO_2 production rates included on plot- imply degradation mechanism changes





Room temperature lifetime reduced by ~60%

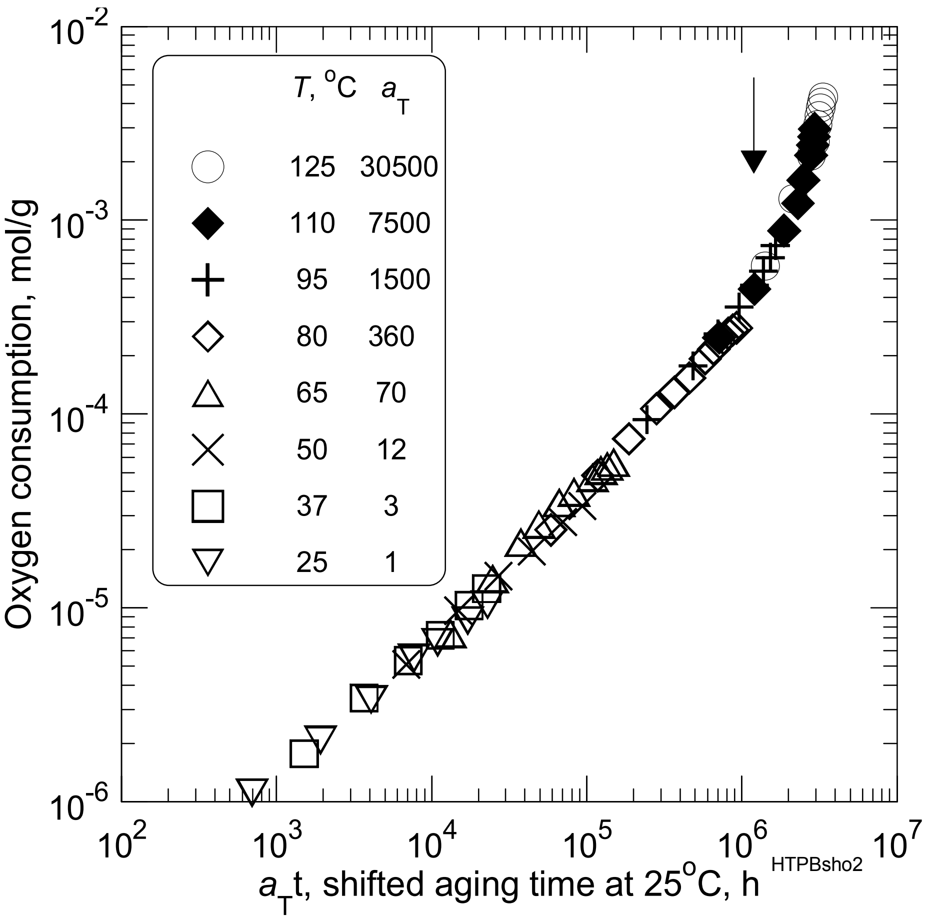
Sandia National Laboratories

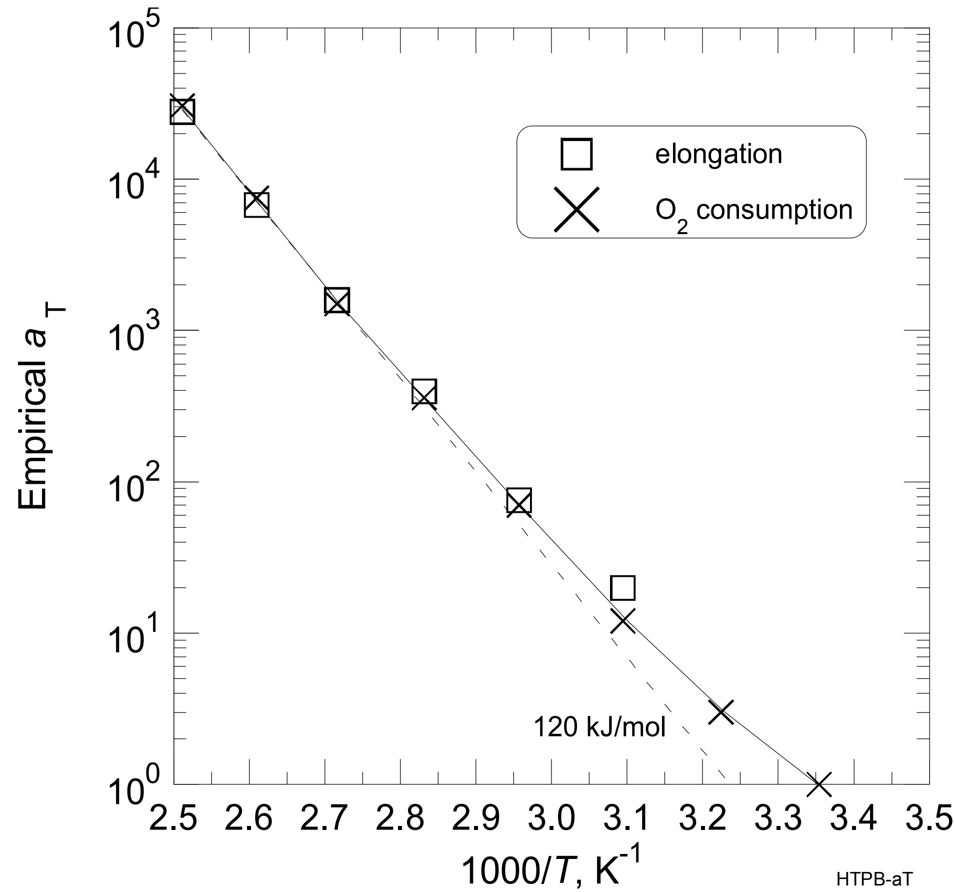
HTPB/IPDI based polyurethane rubber

Ref.- Celina, Graham, Gillen, Assink and Minier, Rubber Chem. Technol., 73, 678 (2000).

t-T superposed O_2 consumption results down to room temperature

Non-Arrhenius for both UOC and elongation results





Note- room temperature lifetimes reduced by ~85%

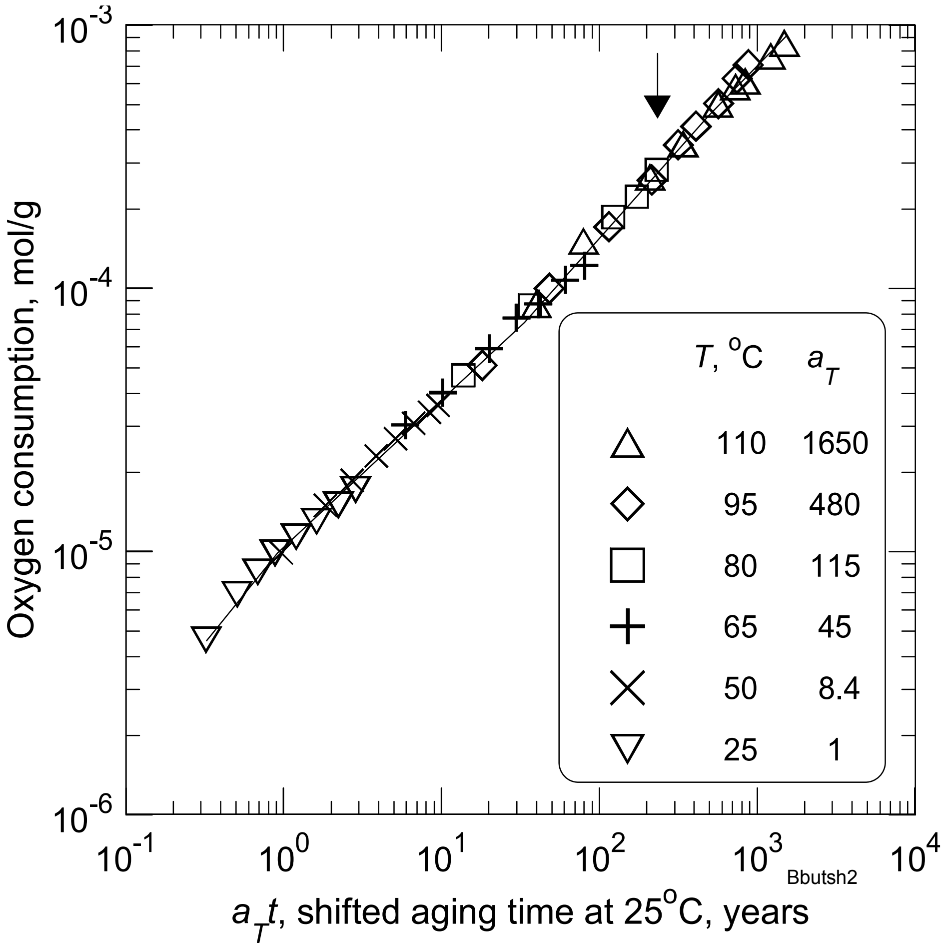
Sandia National Laboratories

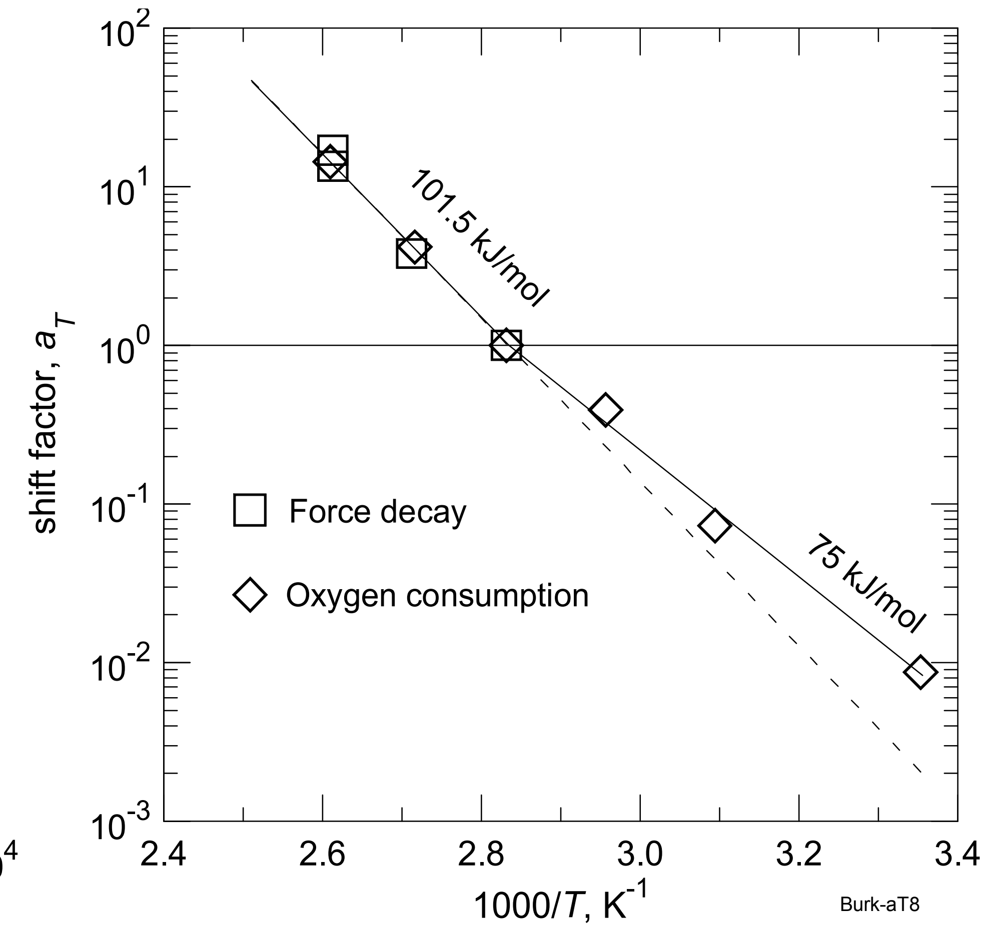
Burke butyl o-ring seal material

Ref.- Gillen, Celina and Bernstein, Polym. Degrad. Stabil., 82, 25 (2003).

t-T superposed O_2 consumption results down to room temperature

UOC indicates a change in E_a in extrapolation regime



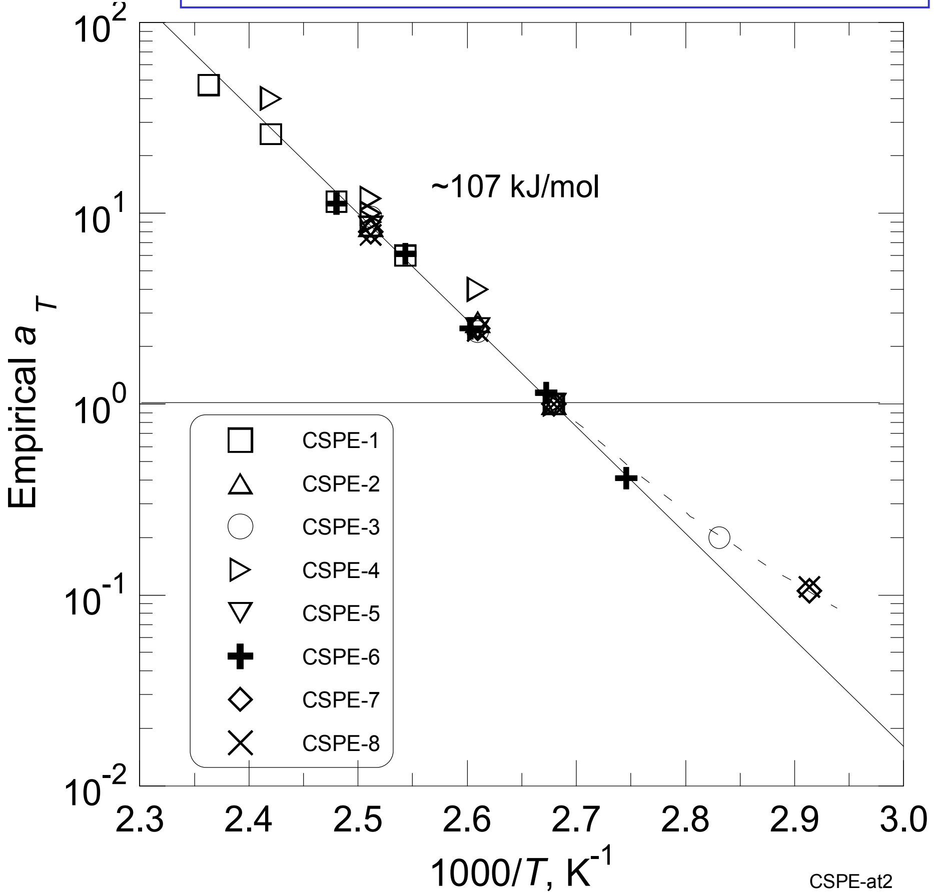


Note- room temperature lifetimes reduced by ~82%

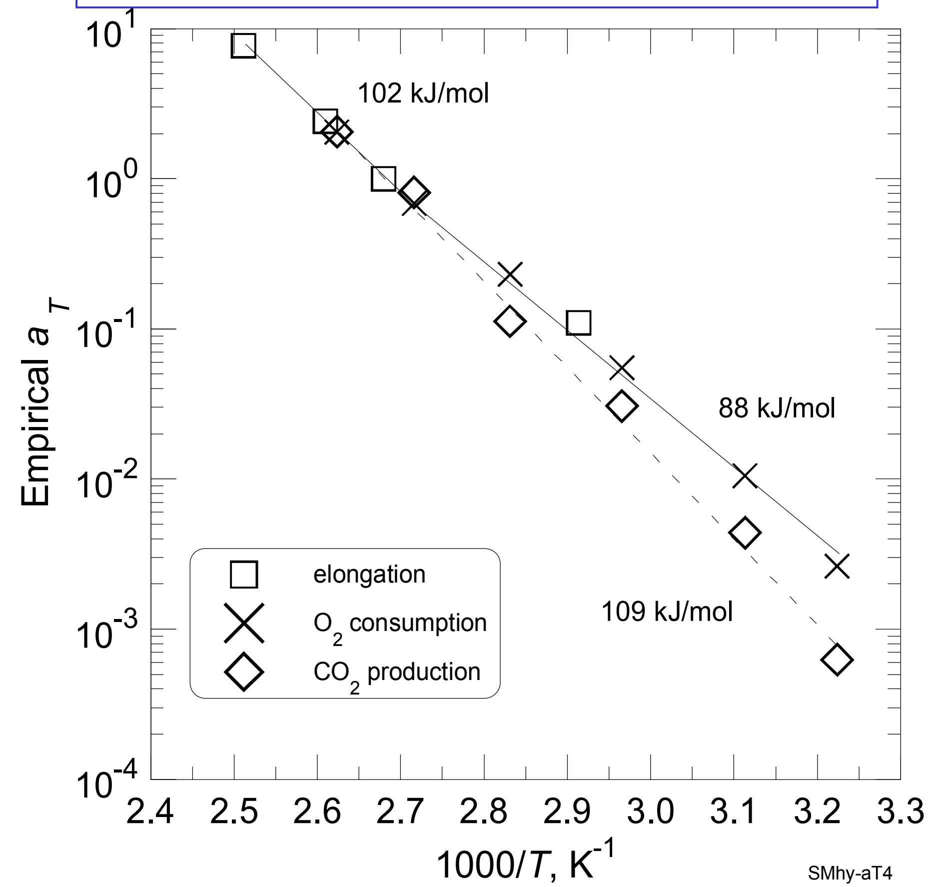
Sandia National Laboratories

Arrhenius plots for chlorosulfonated PE materials

Elongation for 8 different CSPEs



O_2 & CO_2 for Samuel Moore CSPE



- **Similar E_a values at high Ts**
- **Evidence for curvature to lower E_a values at low temperature**

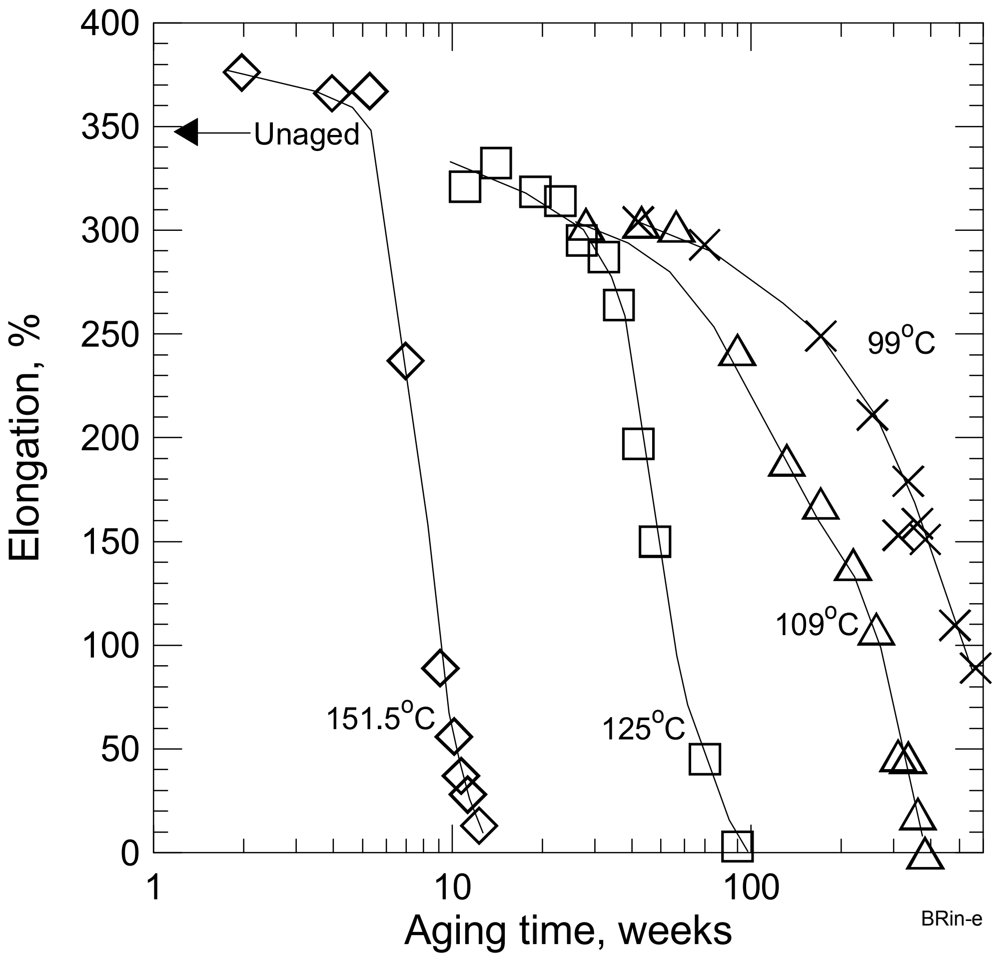
- **Curvature of UOC consistent with curvature of elongation results**
- **CO_2 production has higher E_a**

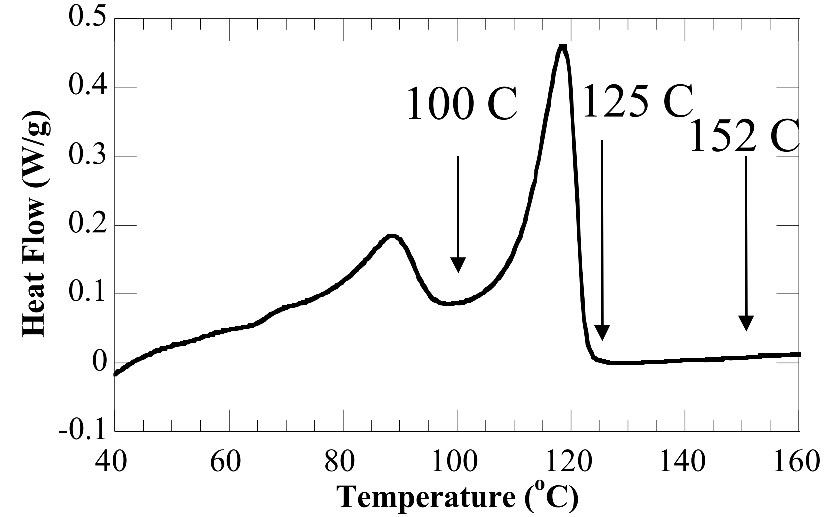
Ref.- Gillen, Bernstein and Celina, Polymer Degradation and Stability, 87, 335(2005)

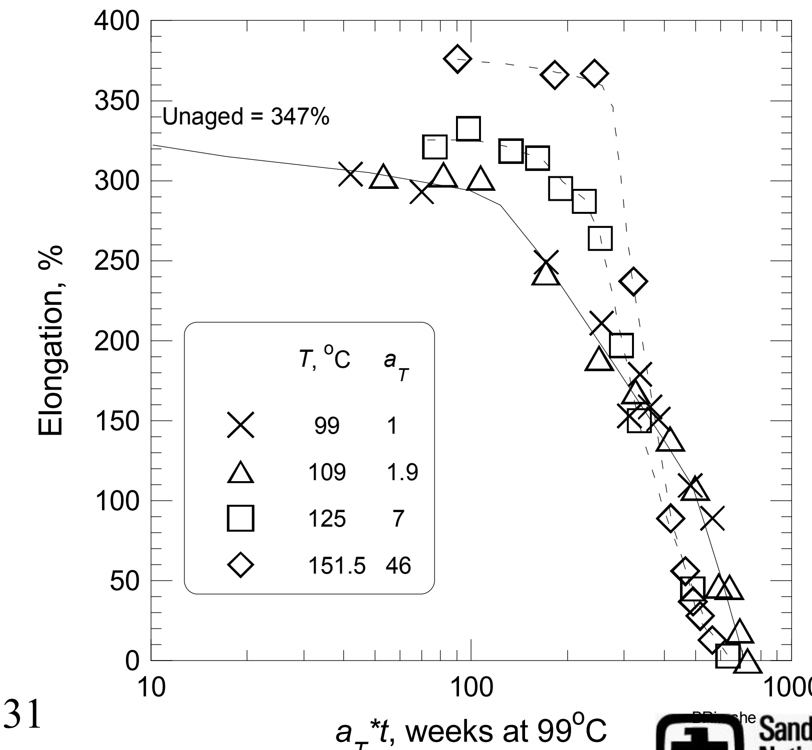
Sandia National Laboratories

Effect of taking data thru T_{mp} point region- examples of non-superposition

Brandrex CLPO insulation





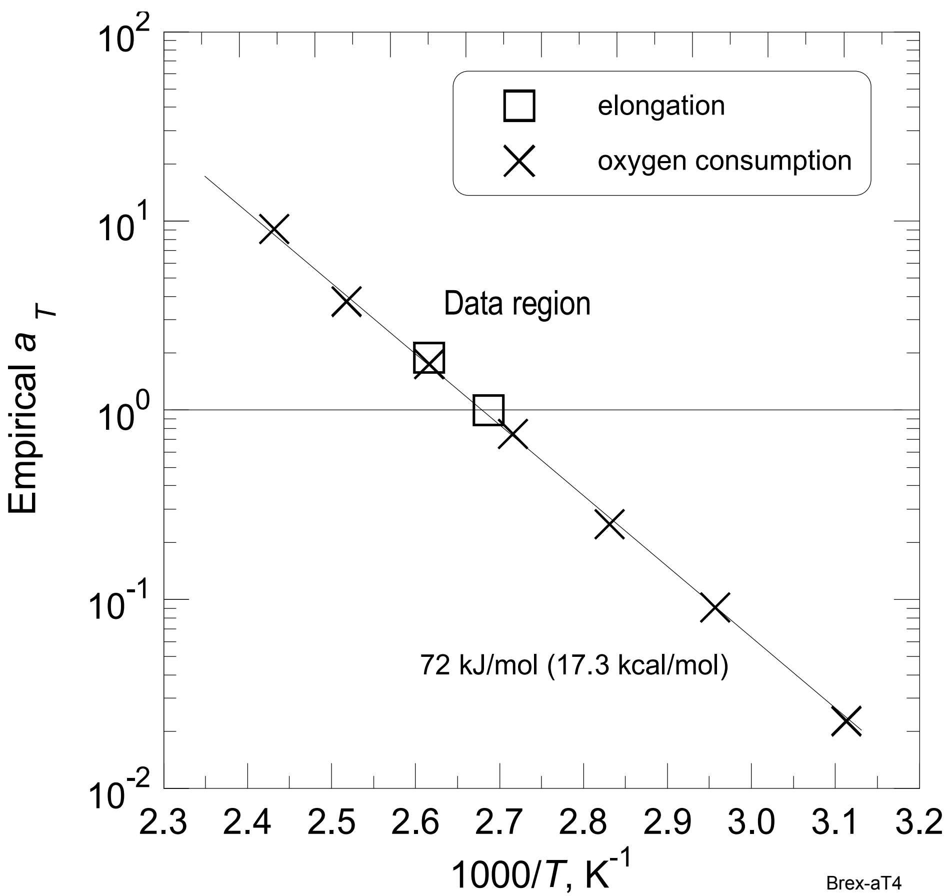


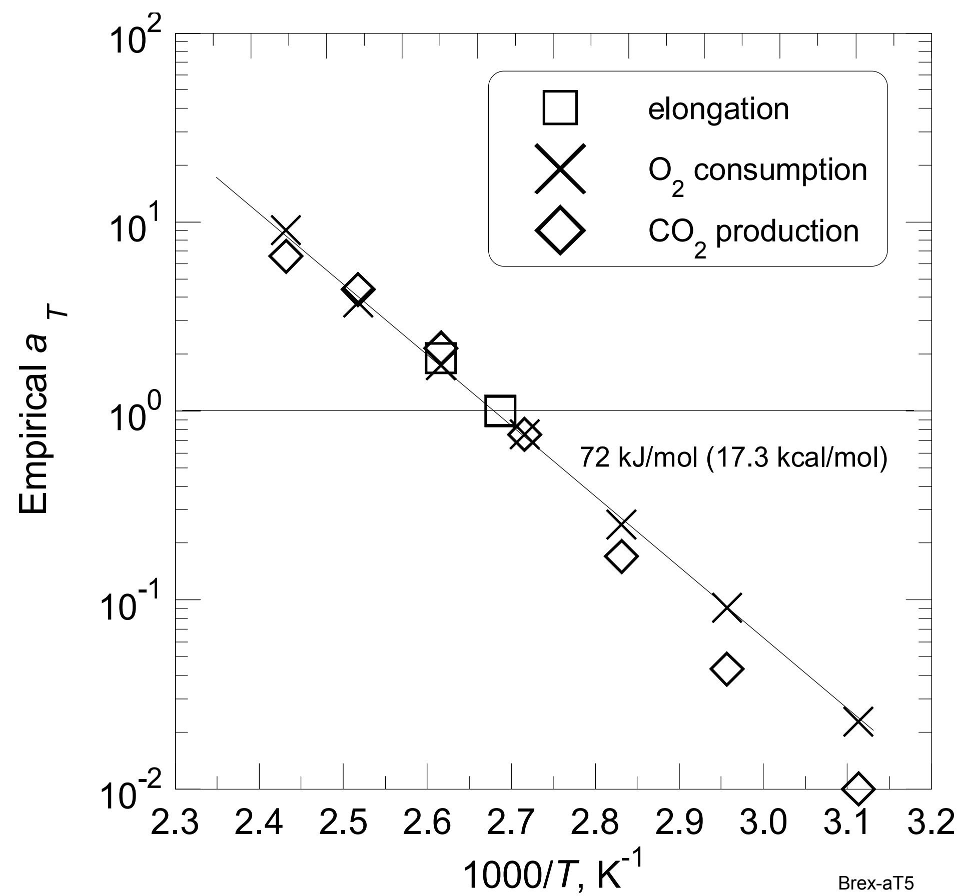
Ref.- Gillen, Assink & Bernstein- SAND Report 2005-7331

Non-superposition implies chemistry changes above T_{mp}

E_a for elongation at 99°C & 109°C is consistent with O_2 consumption results but overlap region small

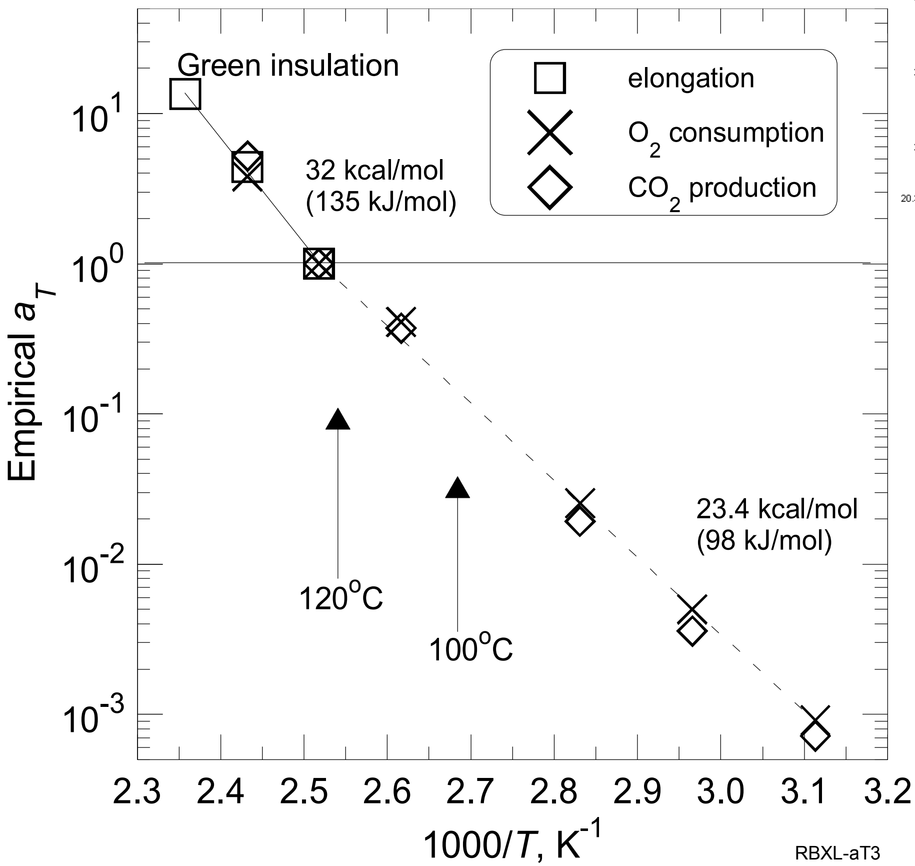
E_a for CO_2 is slightly higher indicating some changes in the oxidation chemistry are also occurring below main melting peak

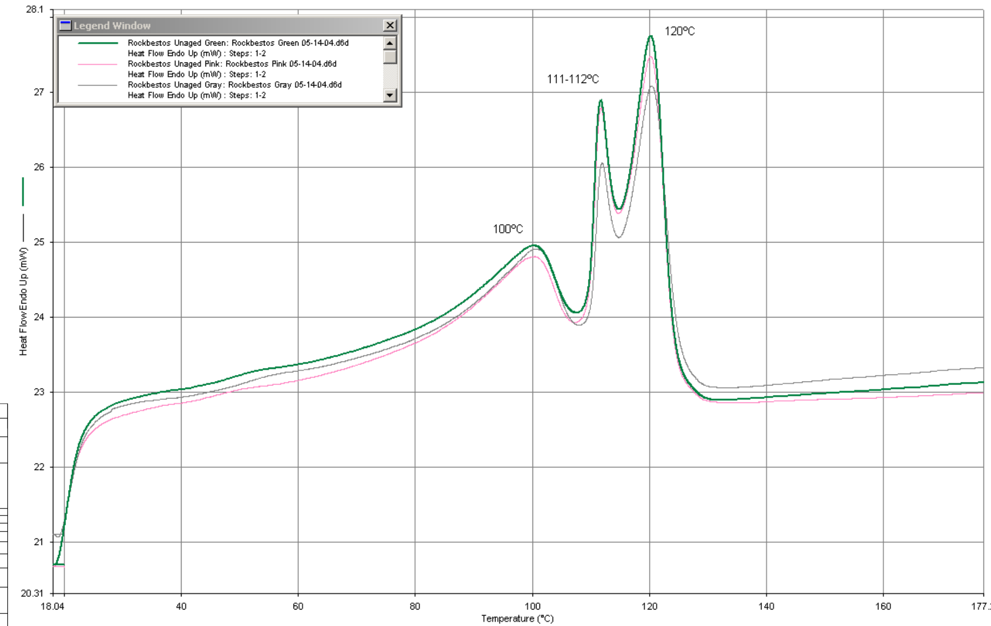




UOC for Rockbestos CLPO

Complex melting region- peaks at 100°C, 110°C and 120°C





Elongation results at 125°C and higher (totally melted) give E_a = 135 kJ/mol (32 kcal/mol)

Oxygen consumption & CO_2 production give E_a ~ 135 kJ/mol above 125°C and ~98 kJ/mol below this temperature

Conclusion- chemistry changes below T_{mp}

Ref.- Gillen, Assink & Bernstein- SAND Report 2005-7331

CONCLUSIONS

- Evidence for chemical changes with temperature change for many materials
- As expected, extrapolating through crystalline melting point region entails major risks
- Wherever possible, data should be taken over an extended temperature range in order to maximize data range and minimize extrapolation distance
- Oxygen consumption approach is one way to achieve this goal for air-aged materials
- E_a usually drops as aging temperature is lowered implying high-temperature extrapolations will often overestimate material lifetimes

Sandia National Laboratories