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Paper # 5

Review of Some Important Issues and Resolutions when Lifetime Predictions of Elastomers are made using Accelerated Aging Techniques

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1974

2004 PREDICTION for 2014

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Elastomers that are expected to last for decades in air environments,
Normal approach- extrapolate results from accelerated aging studies made at higher than ambient environments (e.g., accelerated aging temperatures).

Talk will describe several potential problems and offer some solutions.

1. Changes in degradation chemistry with changes in accelerating temperature- can test by using complete degradation curves in analyses (time-temperature superposition)
2. Diffusion-limited Oxidation (DLO) problems under accelerated aging conditions where DLO effects are not present under ambient aging conditions.
3. Can calculate the importance of DLO effects by estimating or measuring oxygen consumption rates and oxygen permeability coefficients under the accelerating conditions
4. Can experimentally monitor DLO effects using various profiling techniques
5. Can one trust linear Arrhenius extrapolations or is there a better approach? Solution for oxidation-dominated degradation is measurements of oxygen consumption rates at temperatures much lower than accessible to conventional accelerated aging temperatures
6. How does one extrapolate humidity effects?

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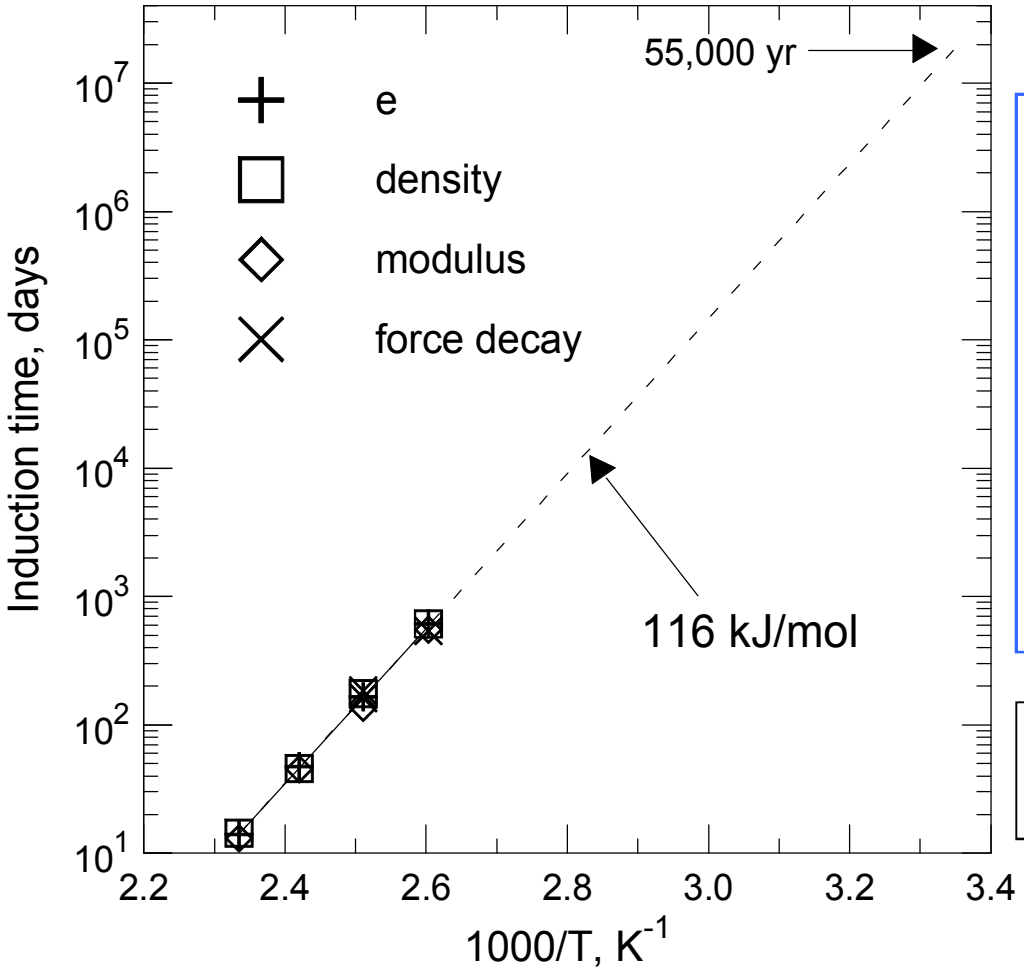
Historic Arrhenius Approach for Lifetime Prediction

- Measure "failure" (induction- time) vs accelerating temperature
- Create Arrhenius plot [$t \sim \exp(-E_a/RT)$] of "failure" times
- Extrapolate to make predictions



EPDM O-RING

- Long life predicted if E_a remains constant
- But long extrapolation
- Only uses a single point on degradation curve
- Therefore little confidence in the prediction

K. T. Gillen, et.al., **Trends in Polymer Science,** 5, 250 (1997).

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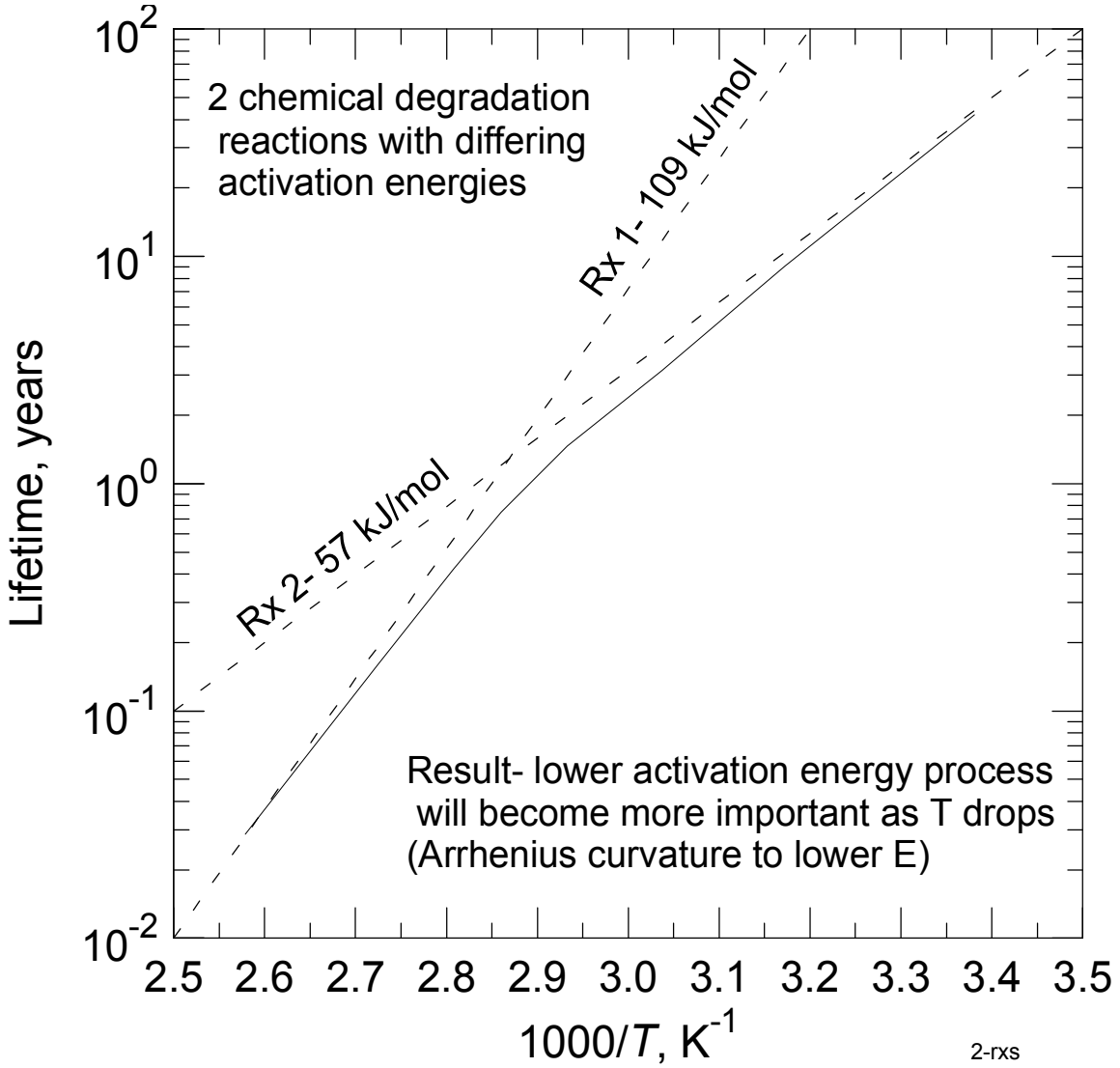
If a new reaction becomes important at low *T*, it will typically have a lower activation energy than the activation energy of the high *T* degradation process.

Therefore, if curvature occurs in Arrhenius extrapolations, expect lowering of activation energy.



Two methods to screen for changing chemistry

1. Time-temperature superposition analyses
2. Obtain data in normal extrapolation regime using sensitive data techniques (e.g., oxygen consumption)

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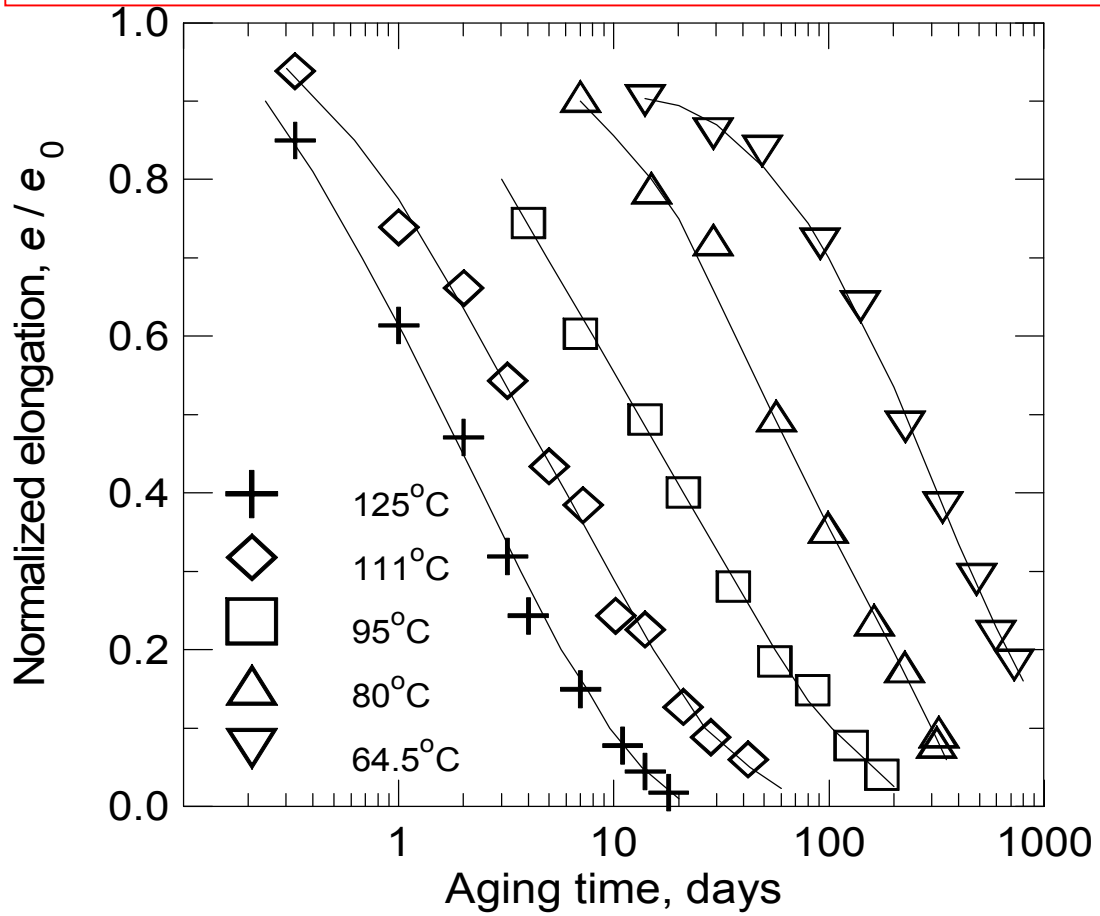
First approach- time-temperature (*t*-*T*) superposition

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 for identical chemistry 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
-minimizes extrapolation

J. Wise, et.al., Polym. Degrad. & Stabil., 49, 403 (1995)

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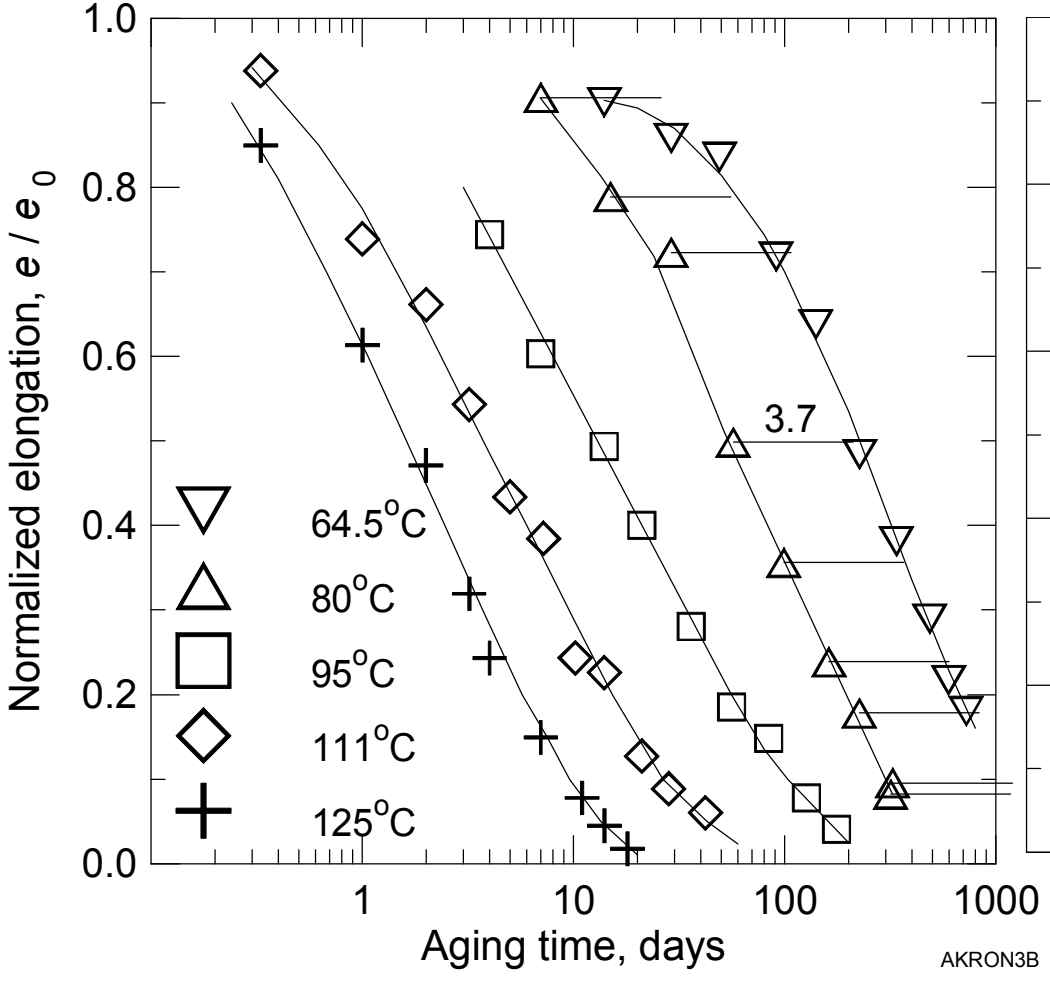
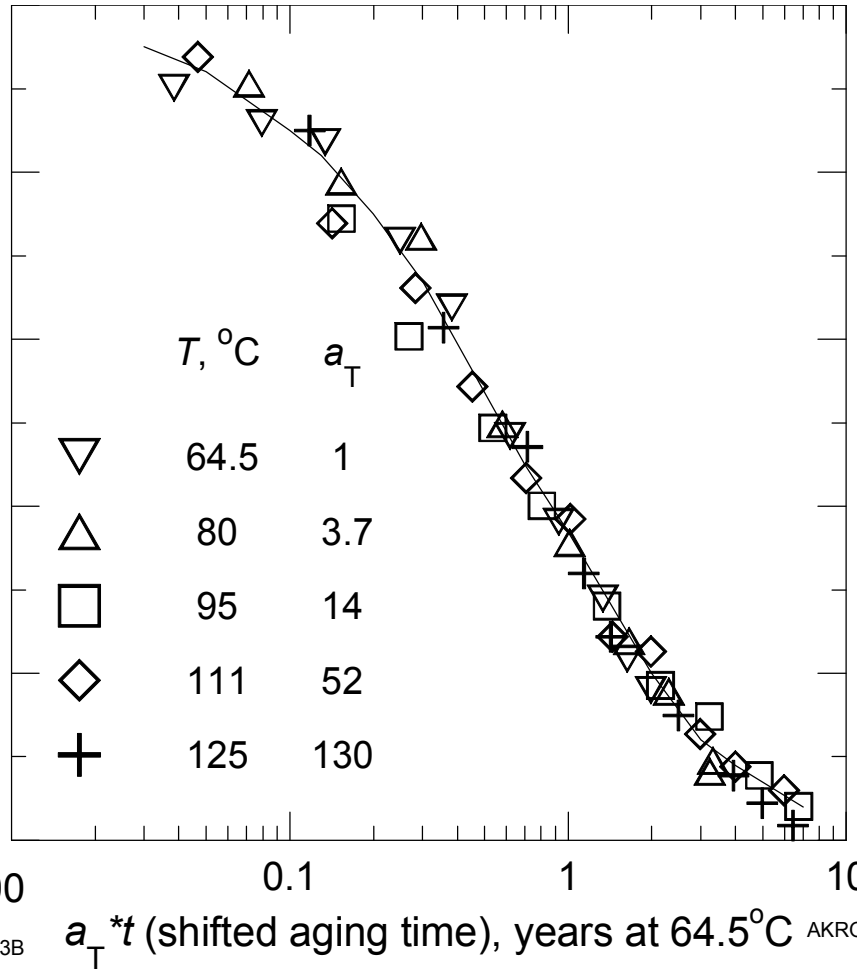
Nitrile- empirical *t-T* superposition at 64.5°C

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

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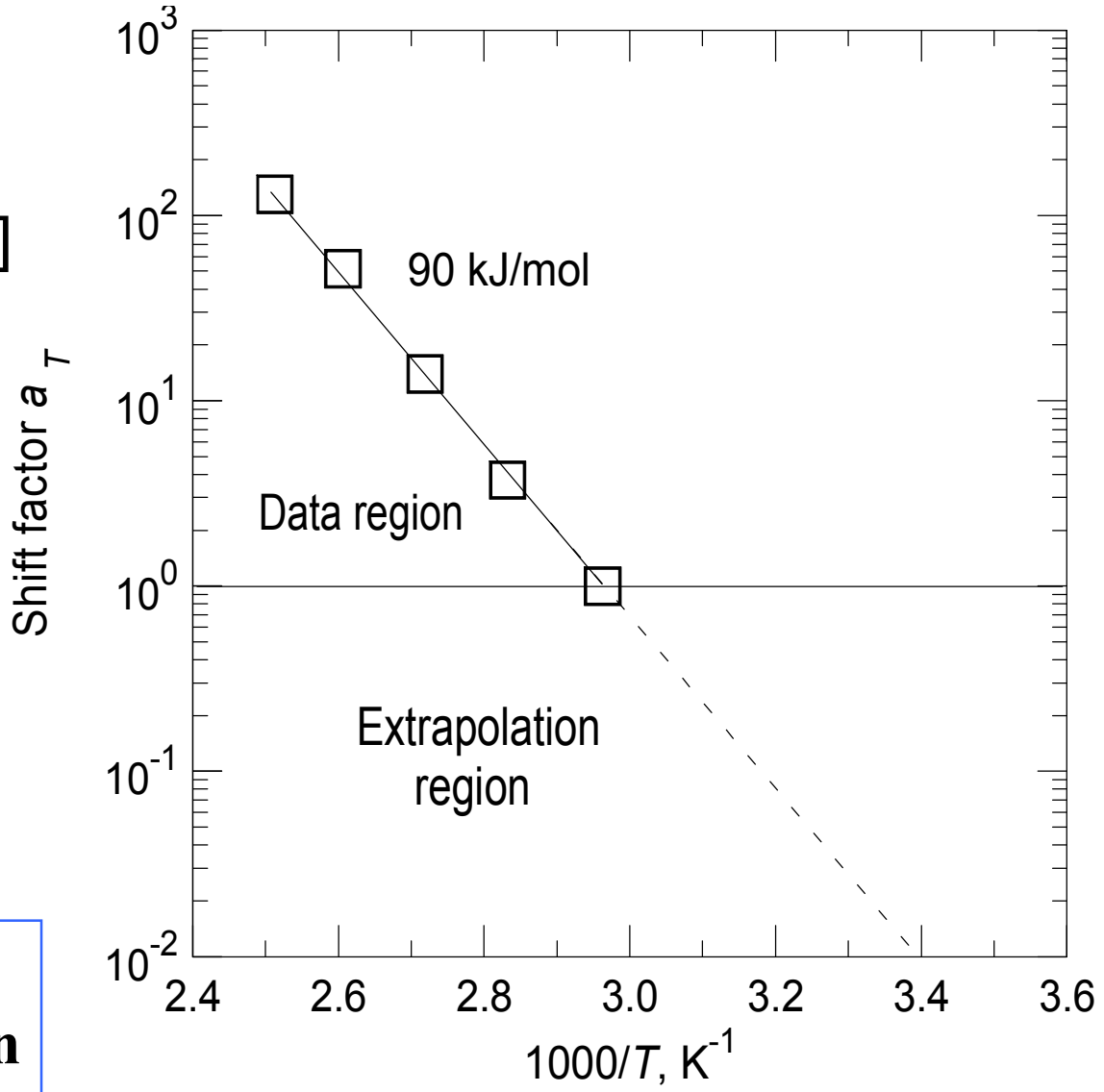
Can Test Various Models on Empirical a_T's

If Arrhenius,

$a_T = \exp[E_a/R][(1/T_{ref})-(1/T)]$

a_T = 1 at 64.5°C (ref. *T*) (NOTE- 2 years aging to minimize extrapolation since probability of slope change increases with extrapolation distance)

Dashed line (a_T < 1) gives unconfirmed extrapolation to lower *T*'s



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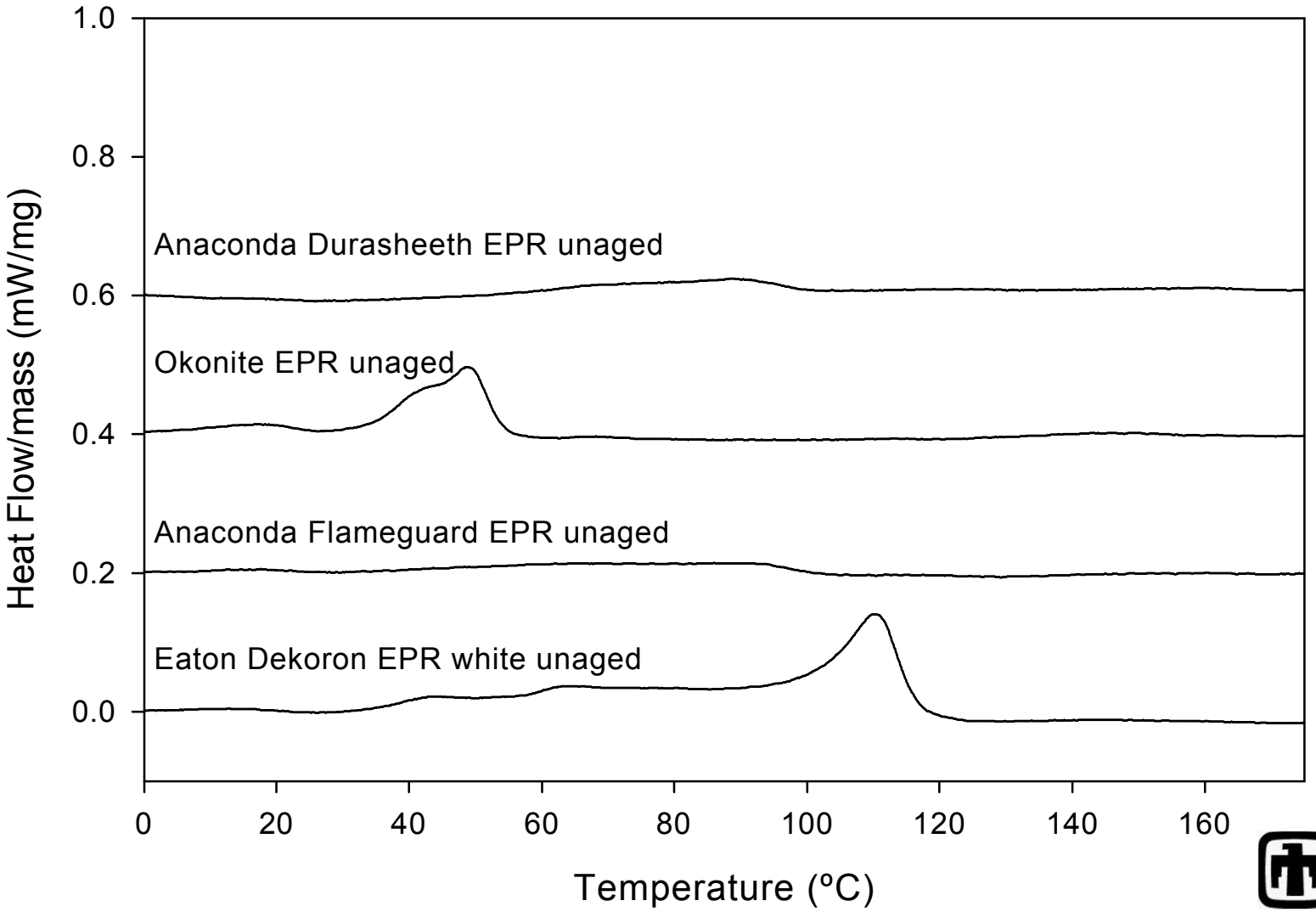
DSC scans of 4 EPR cable materials- the two Anaconda materials show little evidence of crystallinity

-10 to 180°C at 5C/min under Ar - all first runs



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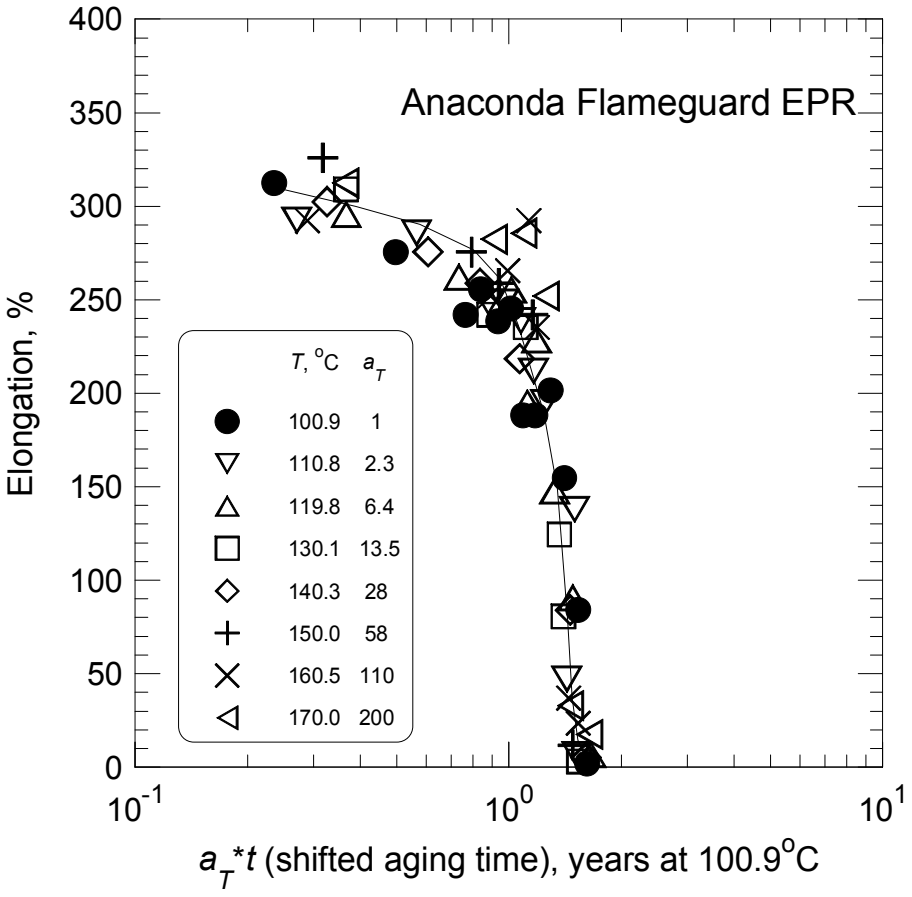
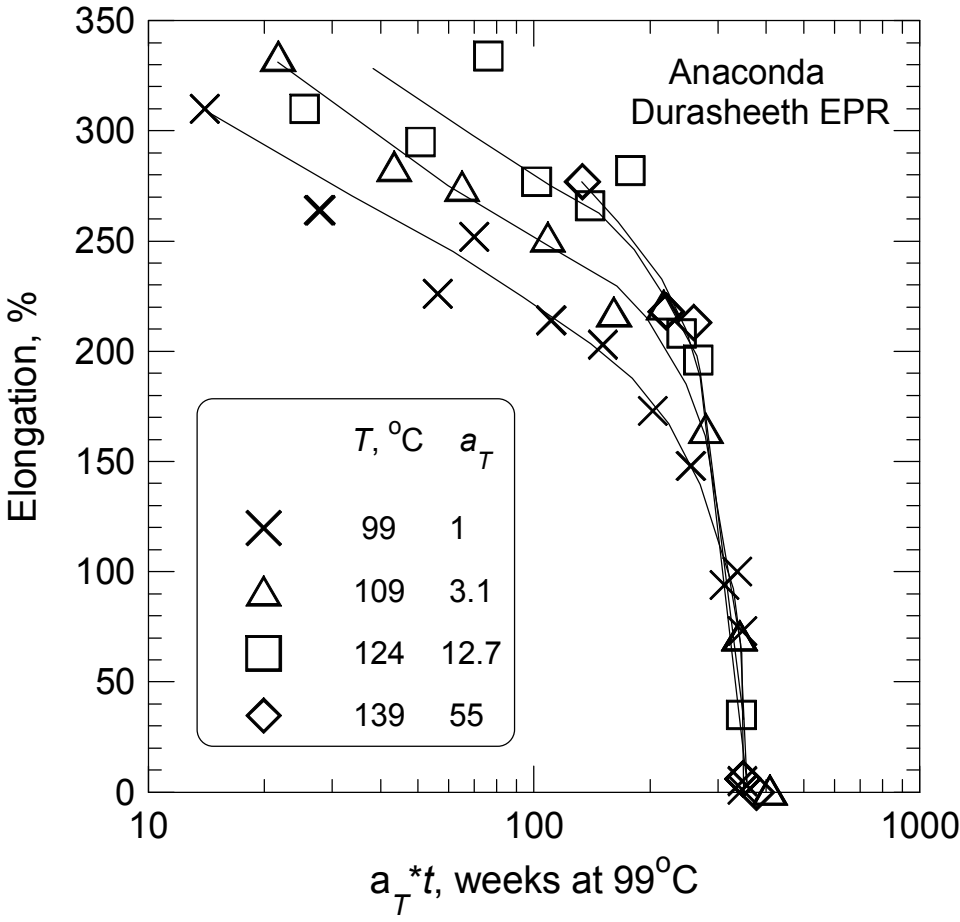
t-*T* superposition of 2 Anaconda EPRs over similar *T* ranges

no evidence of chemistry changes



Evidence of *T*- dependent chemistry



Conclusion- always best to use *t*-*T* superposition analyses

Ref- K. T. Gillen, R. Bernstein, R. L. Clough and M. Celina, Polym. Deg. & Stabil., 91, 2146(2006)

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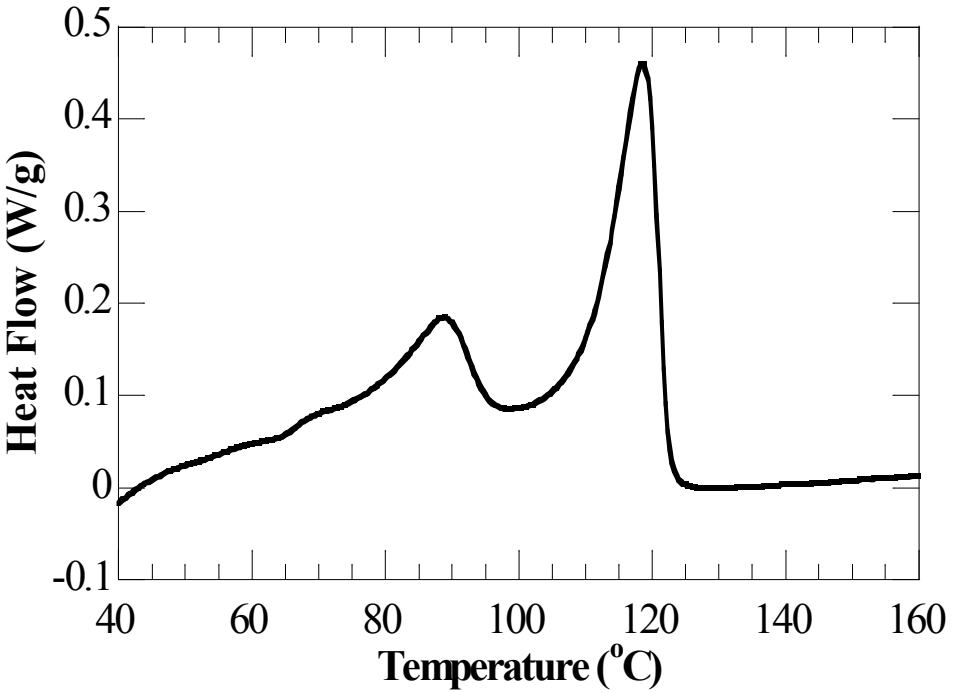
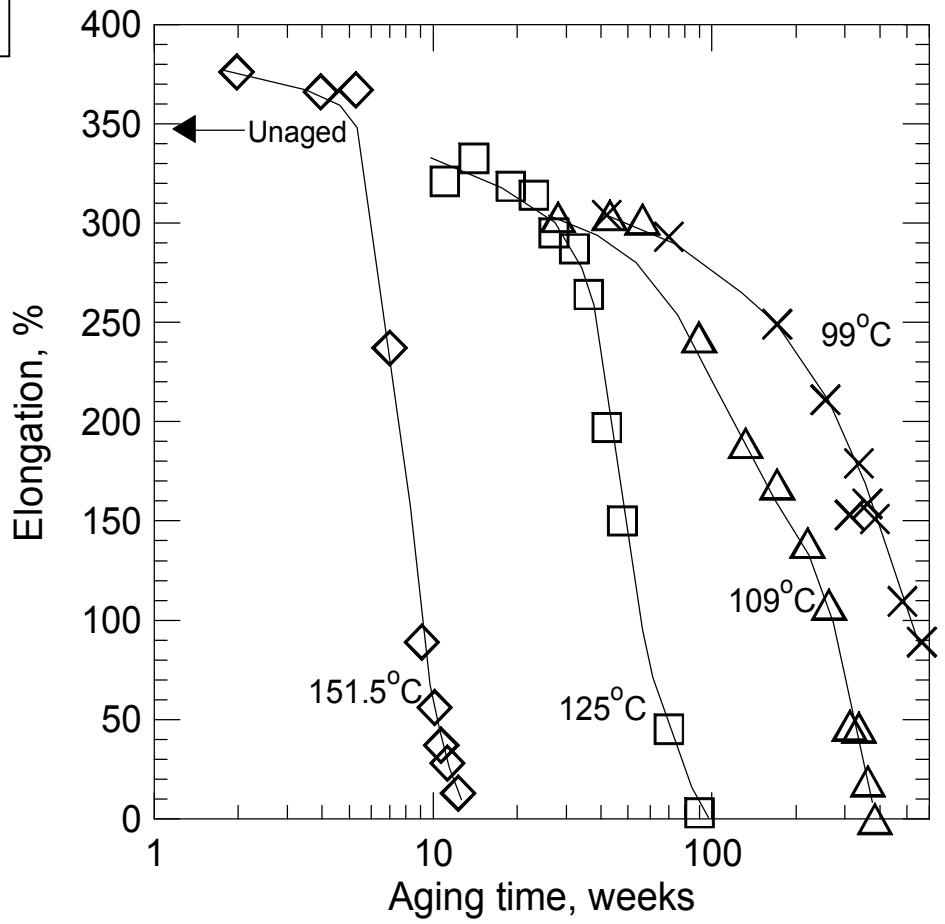
Brandrex XLPO

Might expect chemistry changes as you move across crystalline m. p. region



Elongation data confirms expectation



Ref- K. T. Gillen, R. A. Assink & R. Bernstein, SAND2005-7331 (November, 2005)

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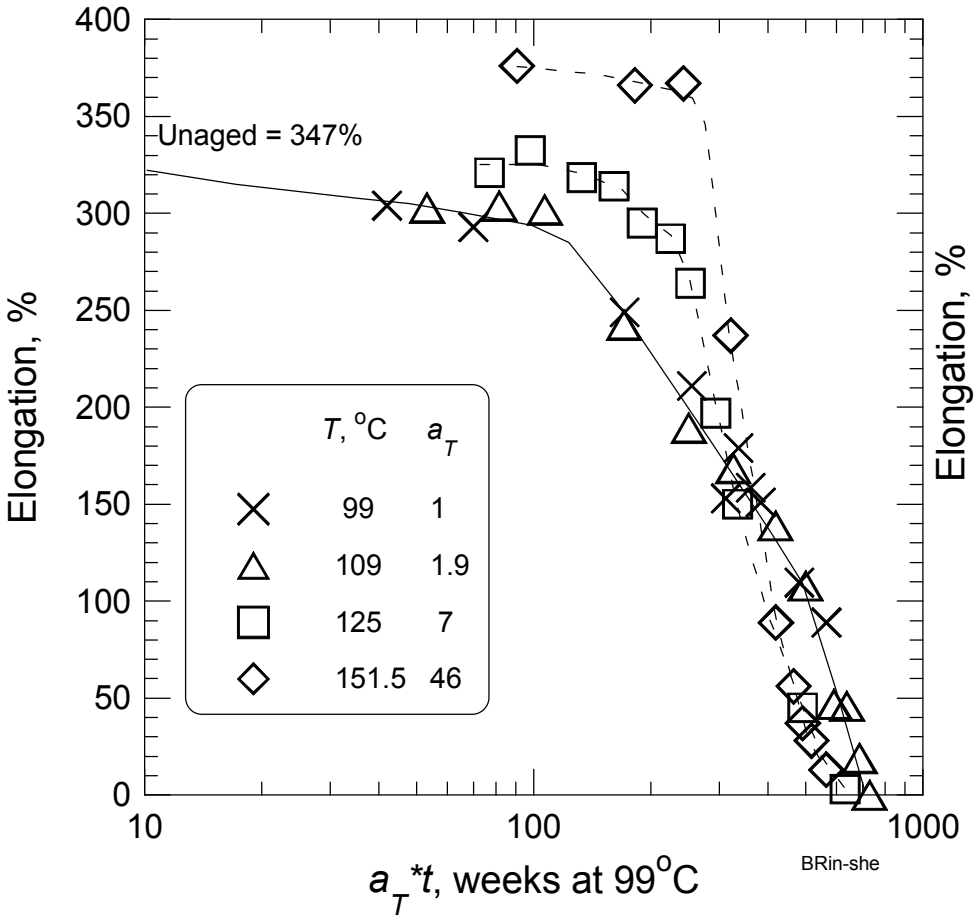
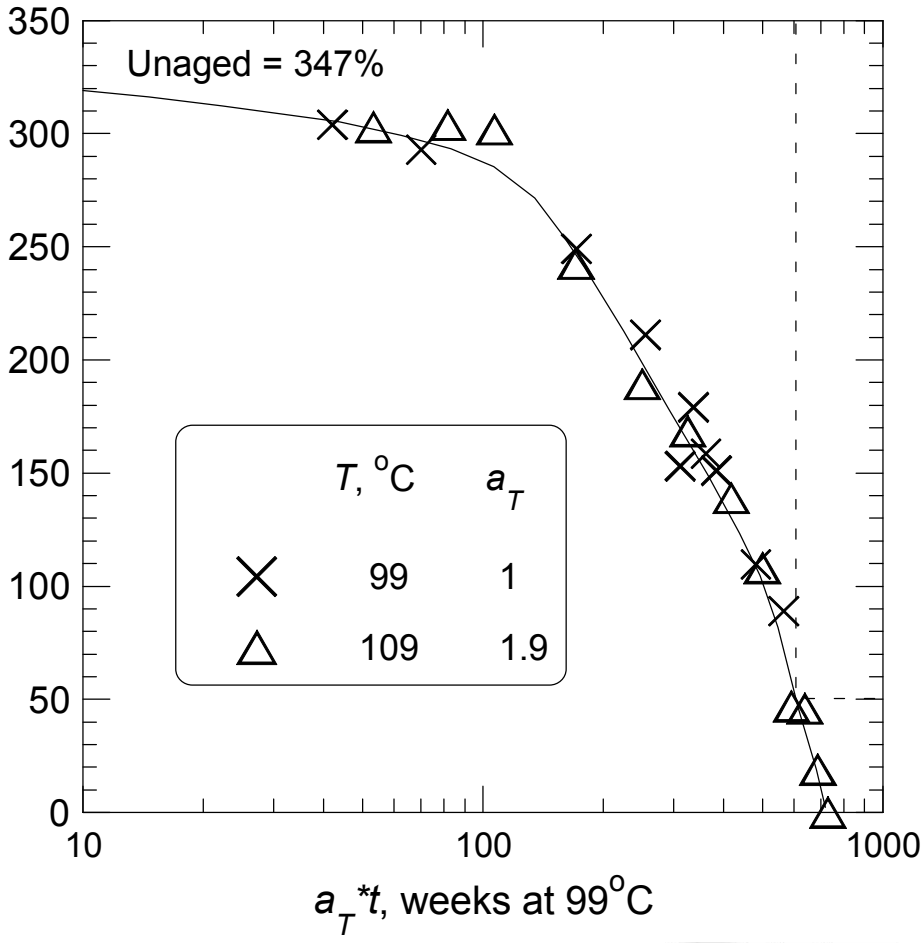
Significant non-superposition for the 4 examined temperatures



Time-temperature superposition is reasonable for 2 lowest temperatures (below main m. p. peak)



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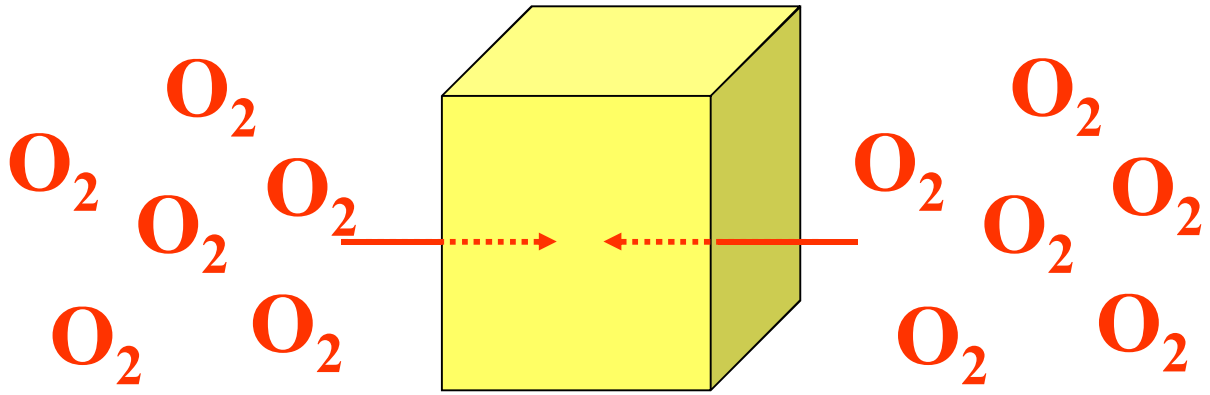
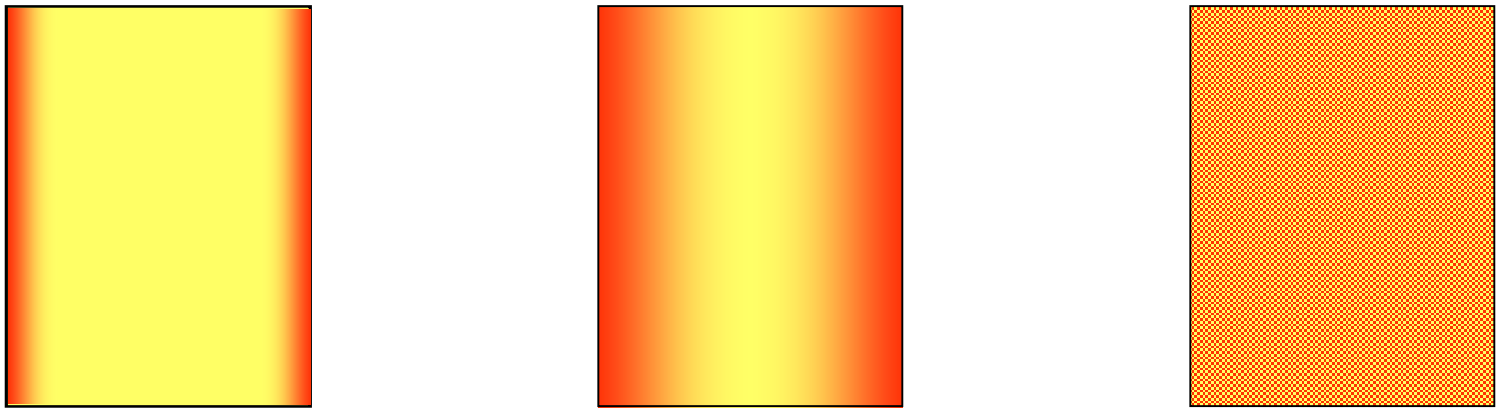
Diffusion-Limited Oxidation (DLO)



rxn rate > diffusion rate

rxn rate < diffusion rate



Heterogeneous

Homogeneous

Since the E_a for reaction is typically much greater than the E_a of diffusion, DLO effects are often important **and temperature dependent** at accelerated aging temperatures but unimportant at ambient temperatures

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Theory for DLO

Ref- K. T. Gillen and R. L. Clough, Polymer, 33, 4358 (1992)

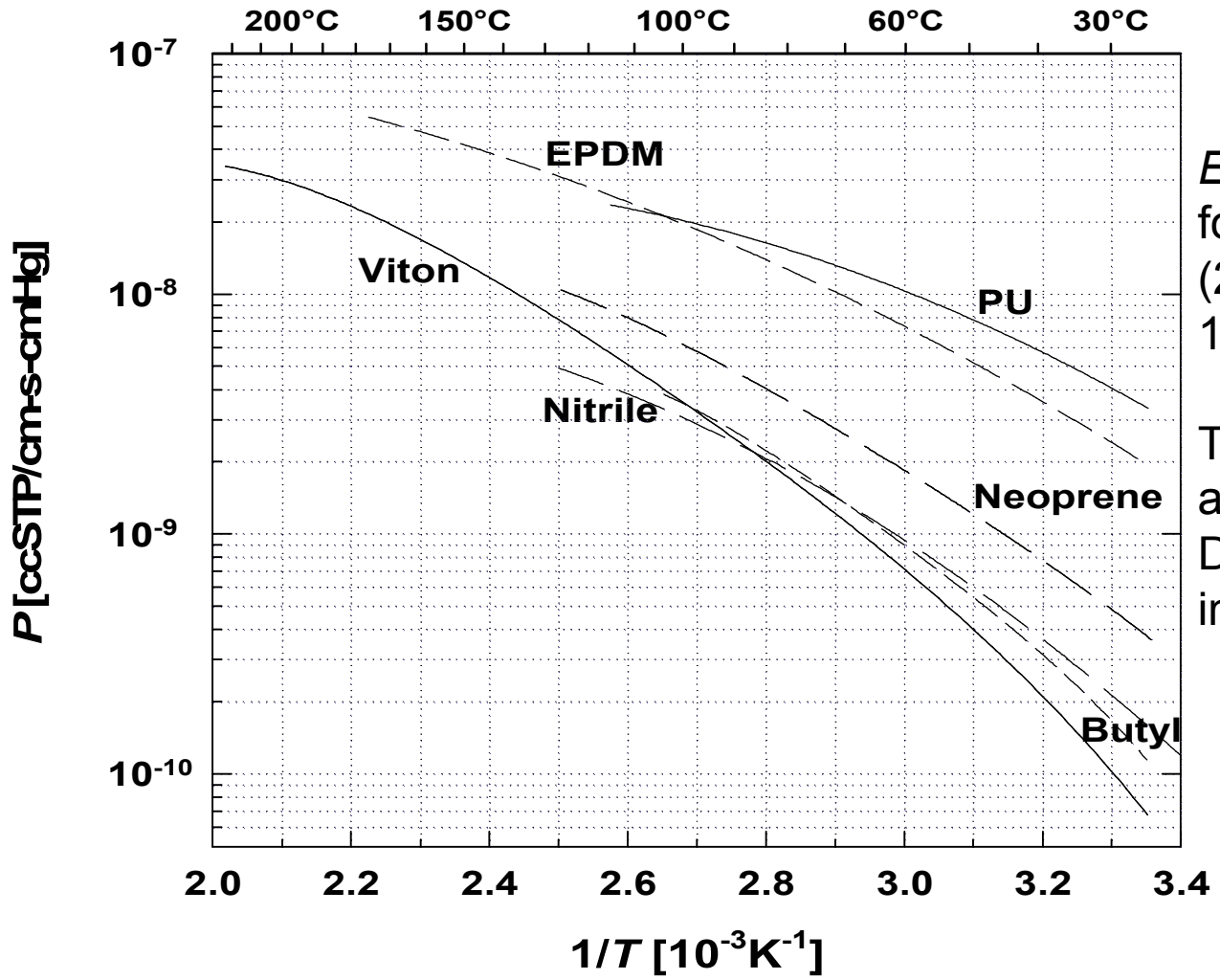
$$L_{90} \sim [2pP_{Ox}/\phi\,]^{0.5}$$

L_{90} = thickness for 90% integrated oxidation
p = surrounding oxygen partial pressure
P_{Ox} = O_2 permeability coefficient
ϕ = oxygen consumption rate

E_a for degradation (ϕ) is typically 70 to 130 kJ/mol

P_{Ox} measurements up to high Ts- experiments need modeling to correct for DLO anomalies

Ref- Celina and Gillen, Macromolecules, **38**, 2754 (2005).



E_a for P_{Ox} is much lower than for oxygen consumption (27 to 56 kJ/mol at low T; 14 to 30 kJ/mol at high T)

Therefore L_{90} will decrease as aging temperature raised so DLO will become less important as aging T drops

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Experimental Probes of DLO

Among the most useful- Micro-FTIR & Modulus Profiling

Modulus Profiling- ~50 μm resolution, ~5% accuracy

References

K. T. Gillen, R. L. Clough and C. A. Quintana, "Modulus Profiling of Polymers", Polym. Degrad. & Stabil., 17, 31 (1987)

K. T. Gillen, E. R. Terrill and R. W. Winter, "Modulus Mapping of Rubbers Using Micro- and Nano-Indentation Techniques", Rubber Chemistry and Technology- **Rubber Reviews**. 74, 428 (2001)

CAPABILITIES INCLUDE

- **State of Cure**
  - **uniformity versus position on cross-section**
  - **complex parts**
- **Heterogeneous Aging Effects**
  - **Diffusion-limited oxidation (DLO)**
  - **Surface effects- examples include uv, ozone, copper-catalyzed oxidation**

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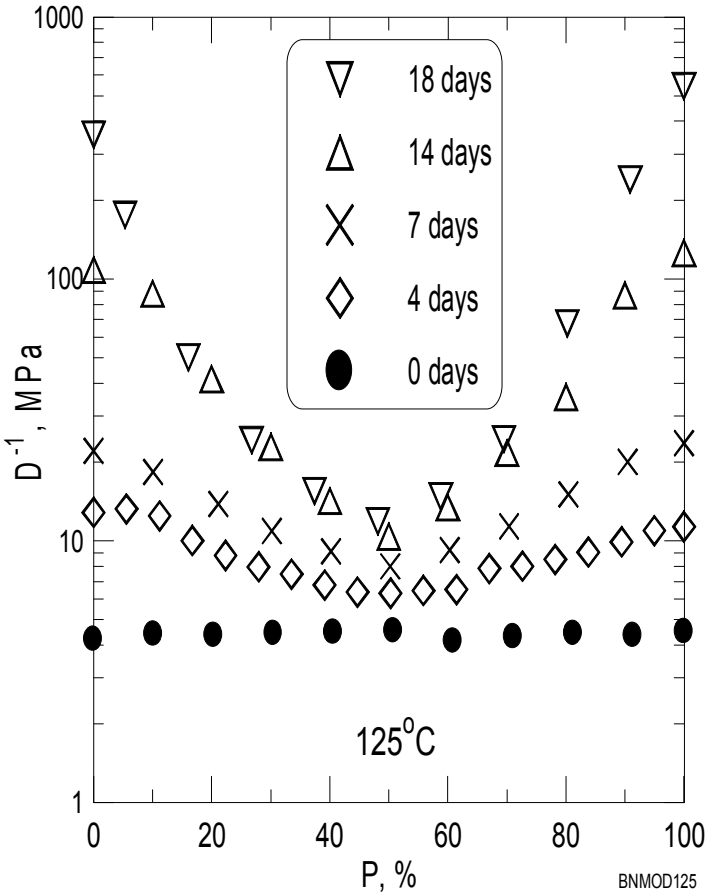
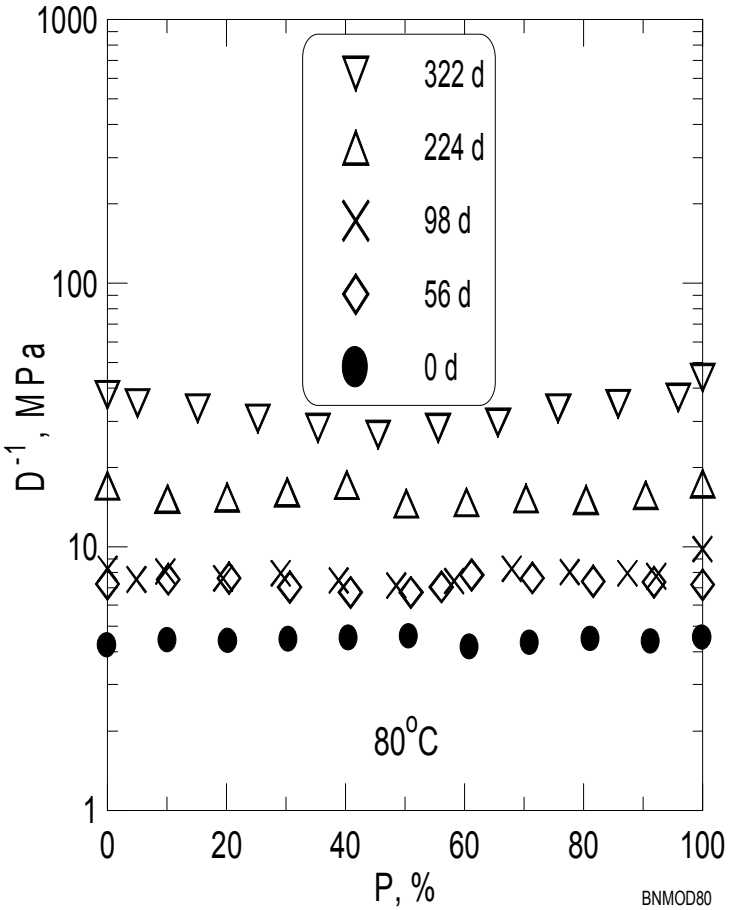
Can see evidence for DLO effects using Modulus profiling

- Allows modulus to be mapped across sample cross-section
- Sandia designed and built- 3 instruments currently exist
  - one at Sandia, one at a commercial US company & one at Akron Research and Development Laboratory (Analytical service lab available to anyone)
- Typically get ~50 μm (2 mil) resolution
- Typical accuracy (repeatability) of ~5% even though it is a micro technique
- Apparatus completely automated and computer controlled

Modulus Profiles- at 125°C & 80°C

Profiles taken across 2-mm cross-sections of nitrile rubber





Given important DLO effects, why is elongation Arrhenius?

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

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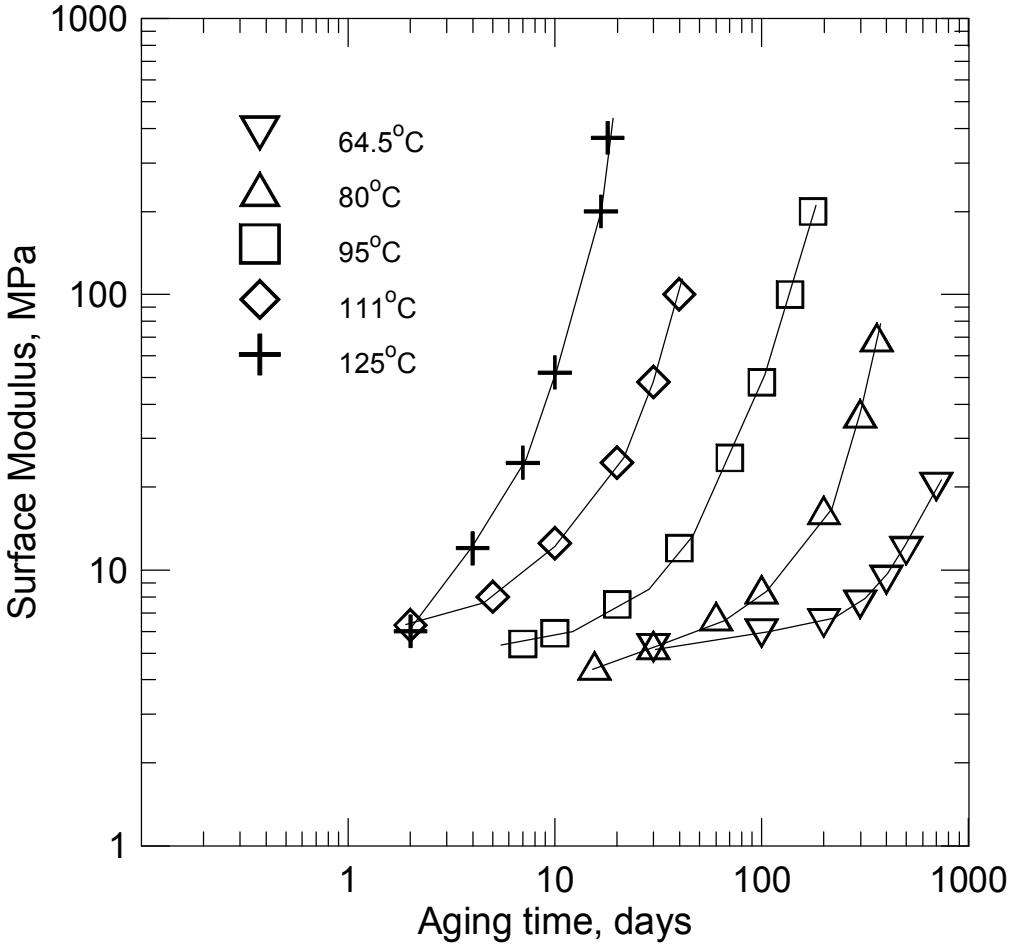
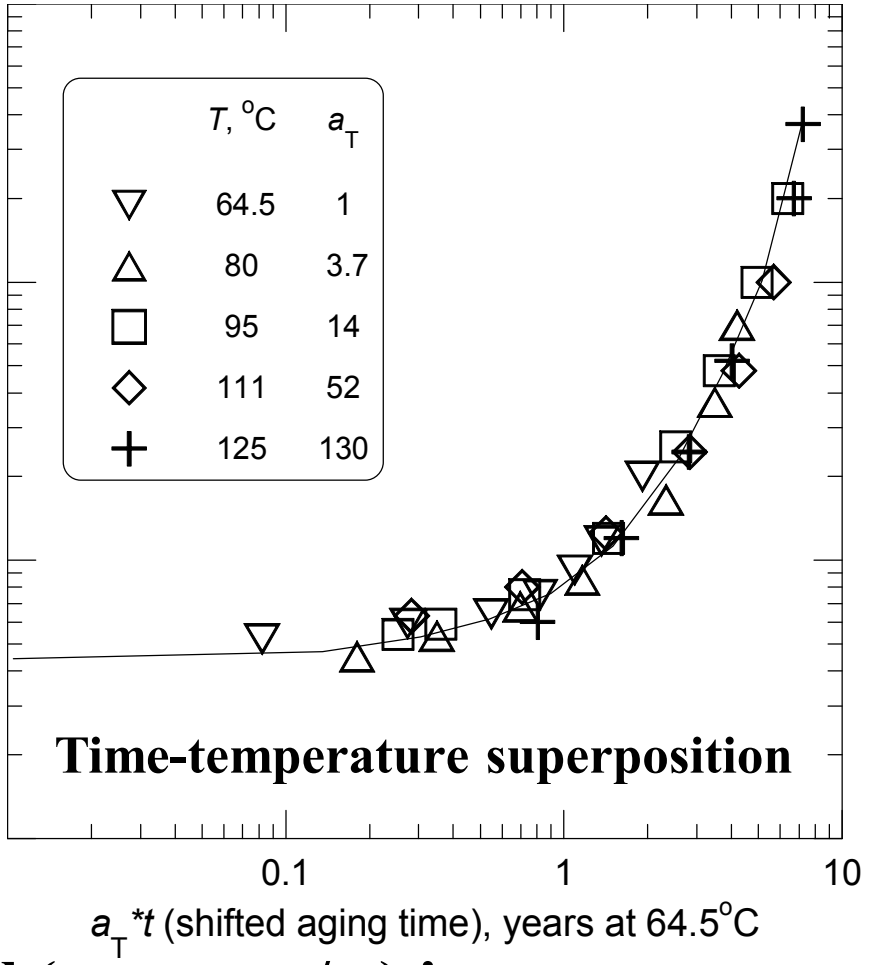
EQUILIBRIUM OXIDATION AT SURFACE





- **Surface values shift with 90 kJ/mol (same as e/e_0) !**
- **Cracks initiate at hardened surfaces, then immediately propagate**
- **Internal material irrelevant to elongation values**

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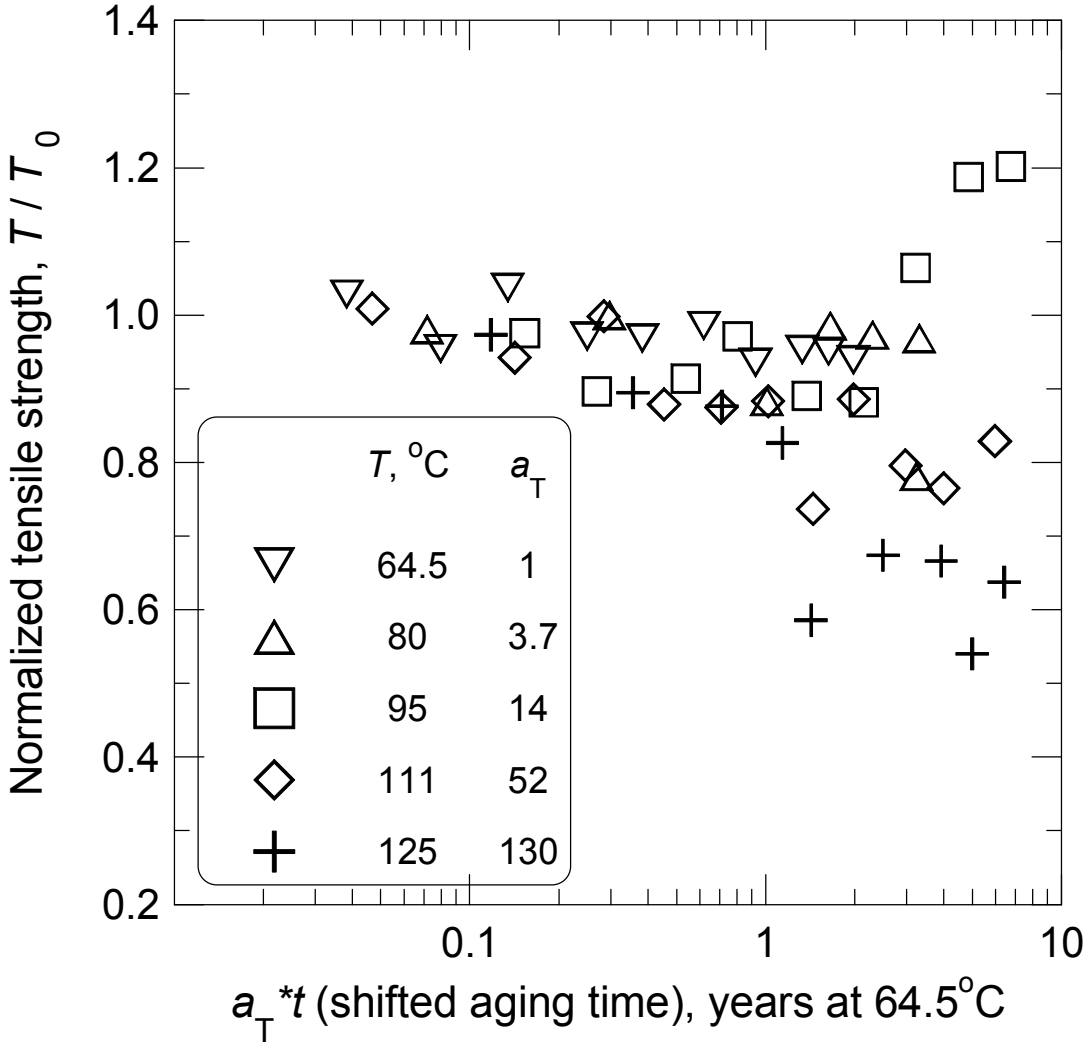
TENSILE STRENGTH- FORCE AT BREAK INTEGRATED ACROSS CROSS-SECTION- DLO EFFECTS IMPORTANT

- **Superposition attempted using a_T's from elongation**
- **Superposition clearly impossible**



When DLO important, any measurement that averages across the cross-section will average oxidized and non-oxidized areas and will therefore be useless for predictive purposes.

Examples- tensile strength, modulus, density, DSC, TGA, OIT, OITP, IR of total X-section, compression stress relaxation, etc.

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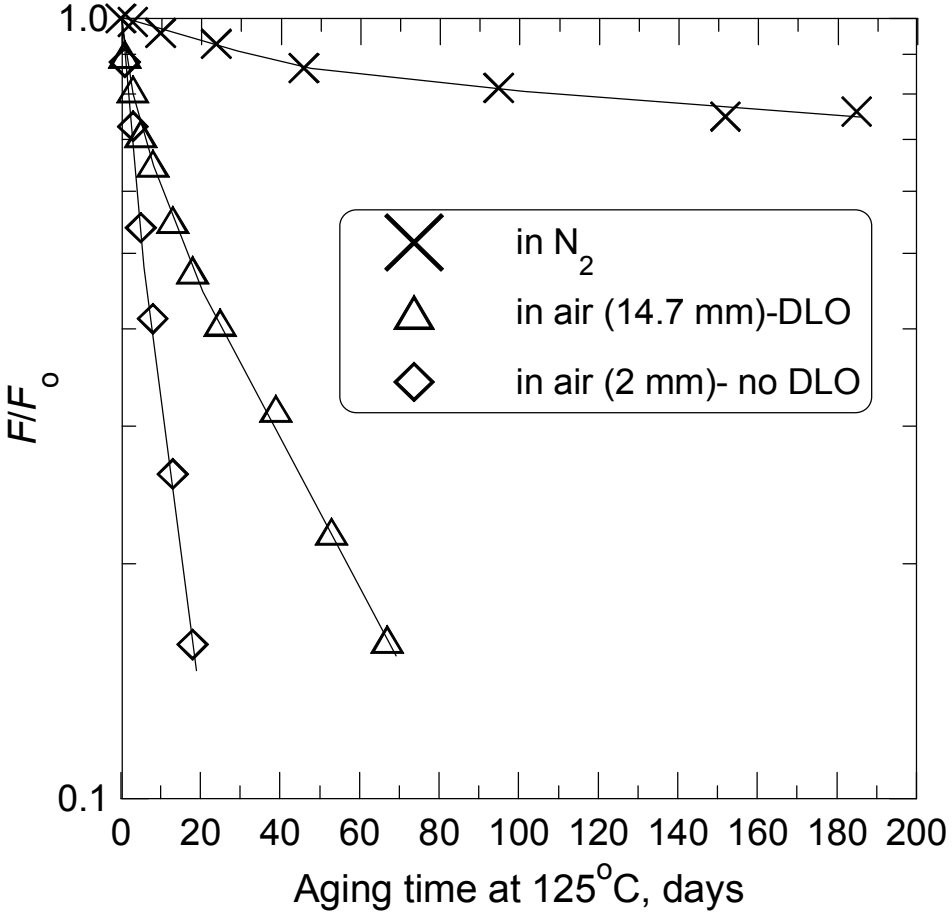
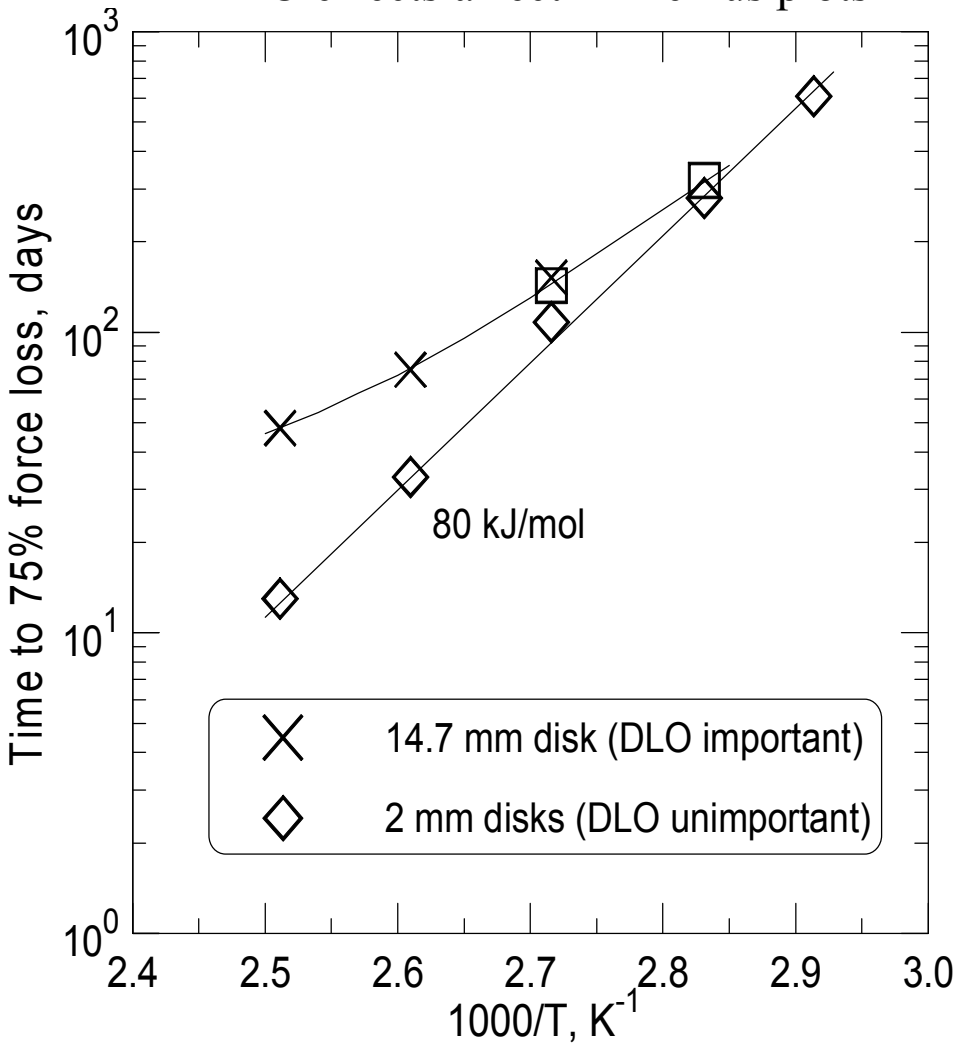
Example- Compression stress relaxation of Parker butyl B612-70

Standard 12.7 mm diam. disk samples- important DLO effects. 2 mm diam. eliminates DLO



DLO effects affect Arrhenius plots



Ref- K. T. Gillen, M. Celina & M. R. Keenan, Rubber Chem. Technol., 73, 265 (2000).

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$$L_{90} \sim [2pP_{Ox}/\phi\,]^{0.5}$$

Rule of thumb- severe mechanical degradation after ~6e-4 mol O_2 /g absorption- this leads to following rough estimates for ϕ versus ~lifetime. Adding rough P_{Ox} estimates gives rough L_{90} estimates.

Lifetime	1 wk	6 mo	70 yr
φ, mol/g/s	1e-9	3.8e-11	2.7e-13
P_{Ox} ,ccSTP/cm/s/cmHg	8e-9	3e-9	2e-10
$L_{90,}$ mm	1.1	3.4	10

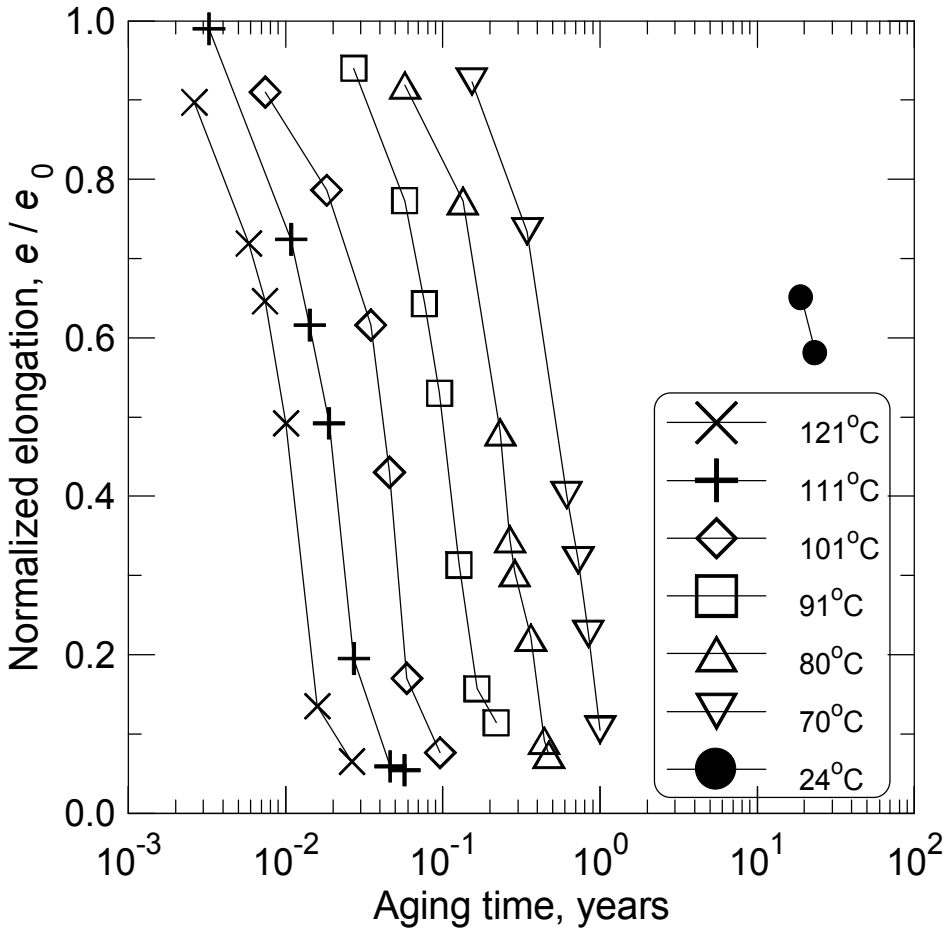
Conclusion- DLO expected for high *T* but should drop out for long lifetimes

We'll see below that 1e-13 mol/g/s can be easily measured!

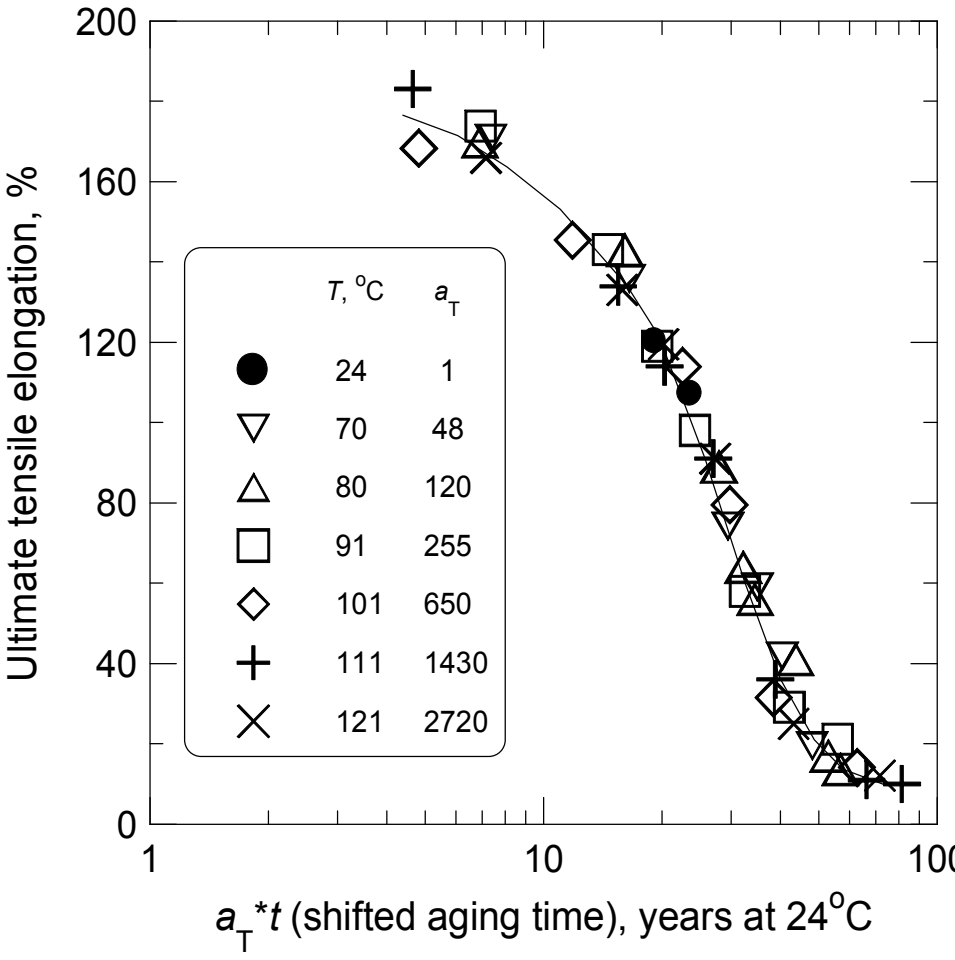
How do you extrapolate to long times?
One way is to find old samples!

We had RT aged samples of Okonite chloroprene from cable studied in 1978-79

Measured *e* values for 19-23 years at ~24°C



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



Ref- K. T. Gillen, R. Bernstein and D. K. Derzon, Polym. Deg. & Stabil., 87, 57(2005).

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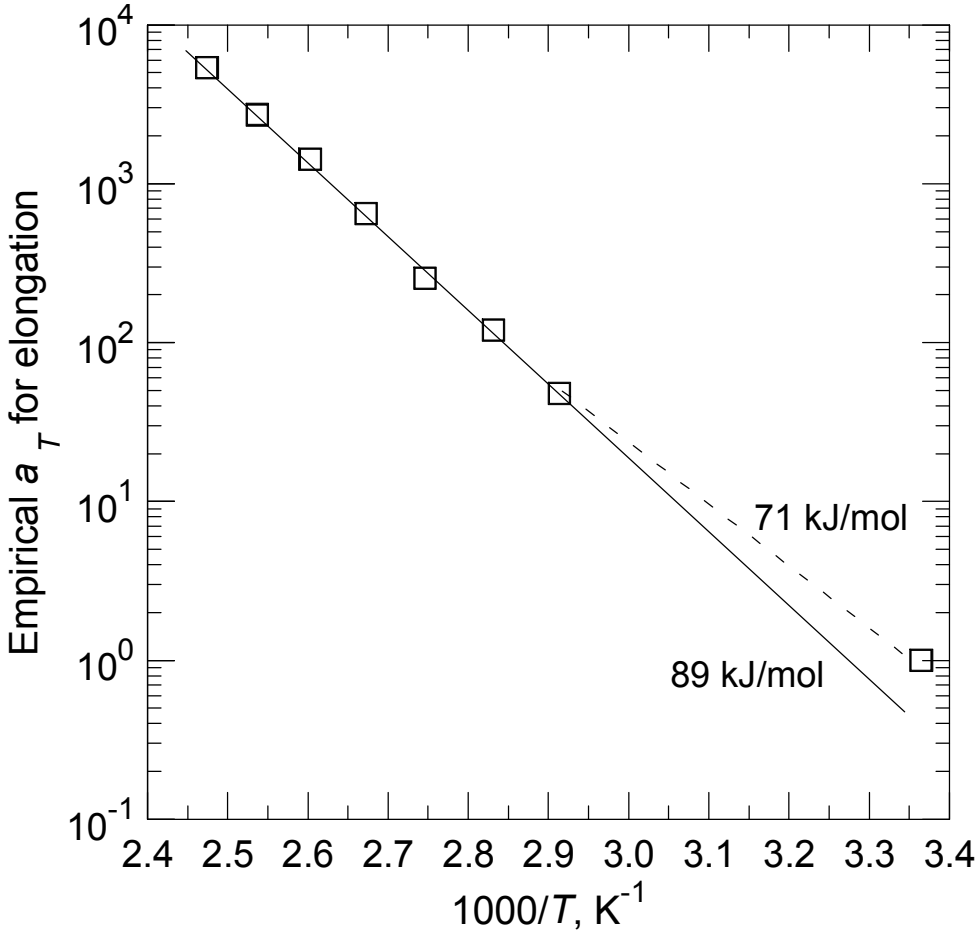
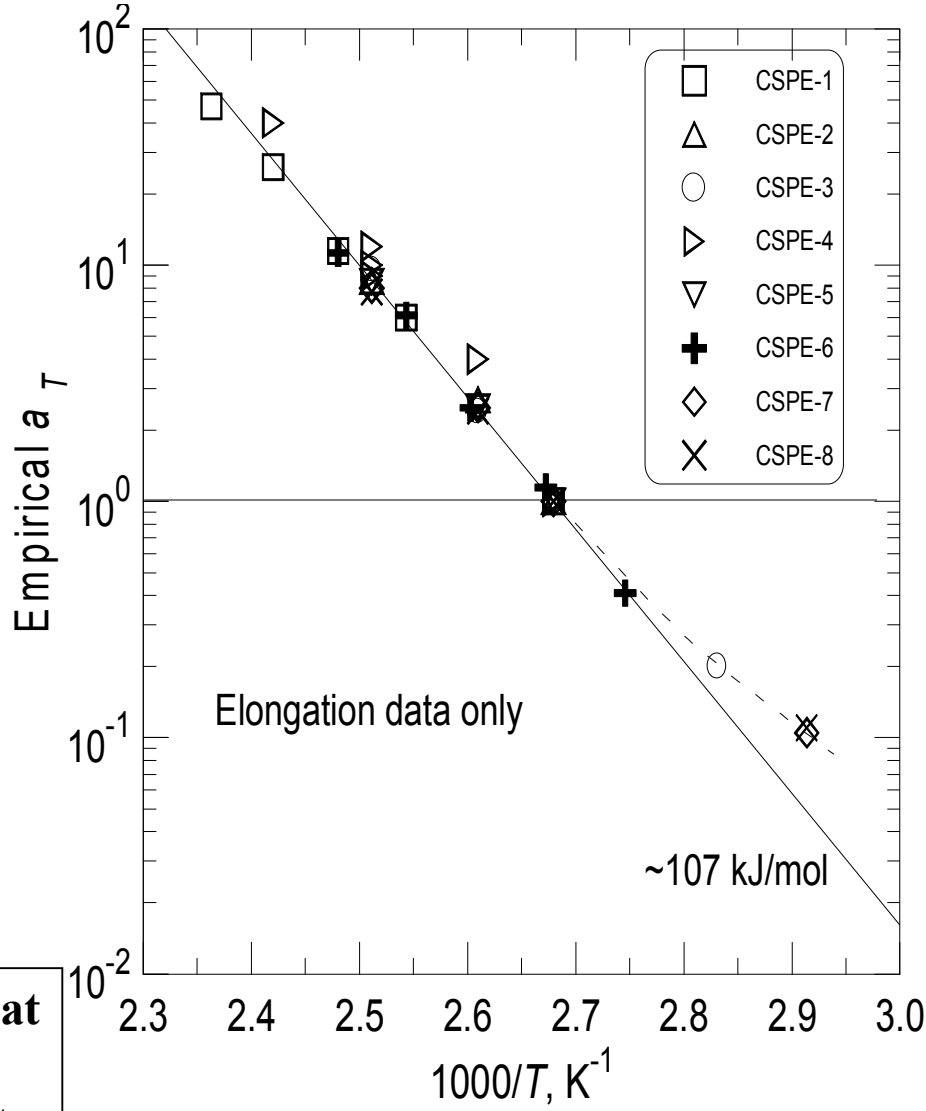
Evidence of drop in E_a from Arrhenius plots of elongation data

Chloroprene result



CSPE results out to 5 years at 70°C



- **Old prediction of 96 years to 50% elongation at 24°C drops to 36 years**
- **Shows sensitivity of extrapolated predictions to slight E_a drop**

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Alternative approach- Oxygen Consumption (ϕ) measurements

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

Seal container with polymer and O_2, then age, then do GC analysis to determine O_2 consumed

Second Approach- Assink RA, Celina M, Skutnik JM, Harris DJ. Polymer 2005;46:11648.

Experimentally similar, but different quantification of oxygen loss in ampoule using a fuel cell detector (Oxzilla system)

- To eliminate DLO effects during ϕ, need to age thin pieces

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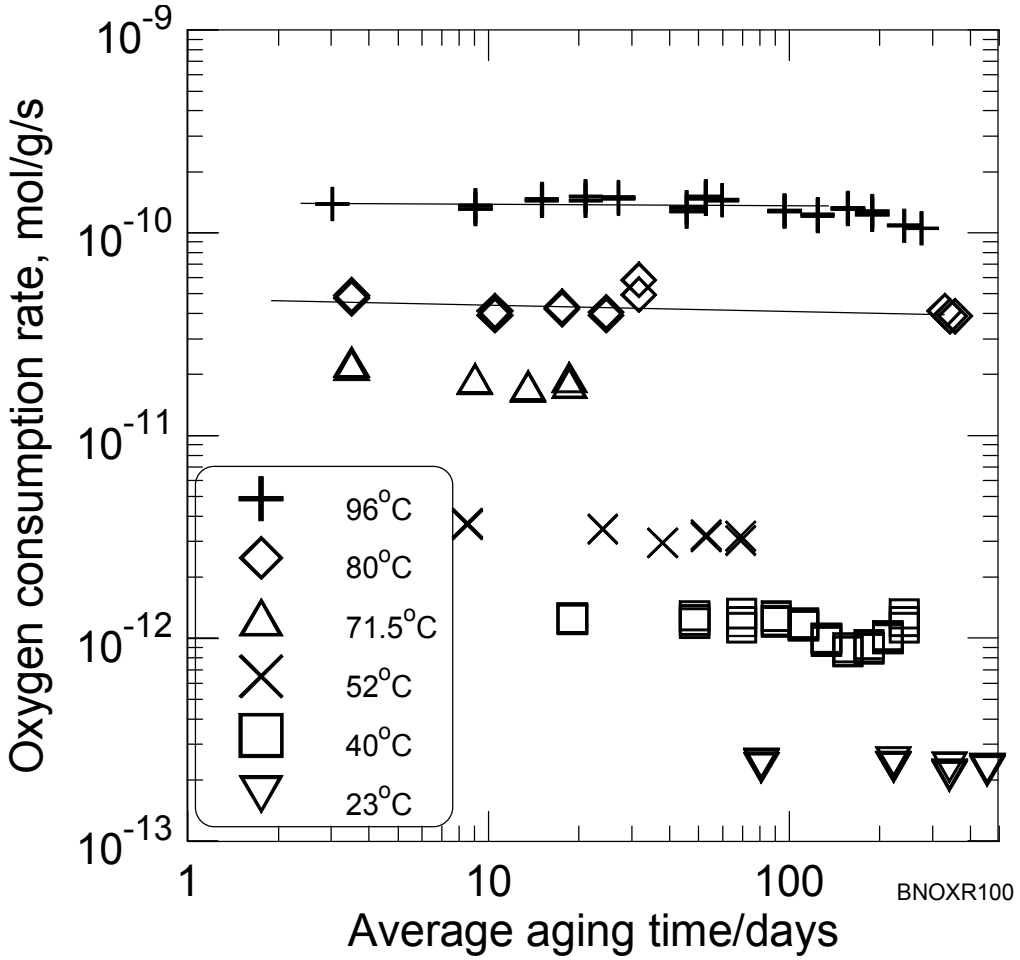
ϕ results for nitrile rubber

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



- results obtained down to room temperature (23°C)
- constant rate at each *T*
- consistent with constant acceleration assumption
- therefore ϕ & *e* data overlap at high *T*

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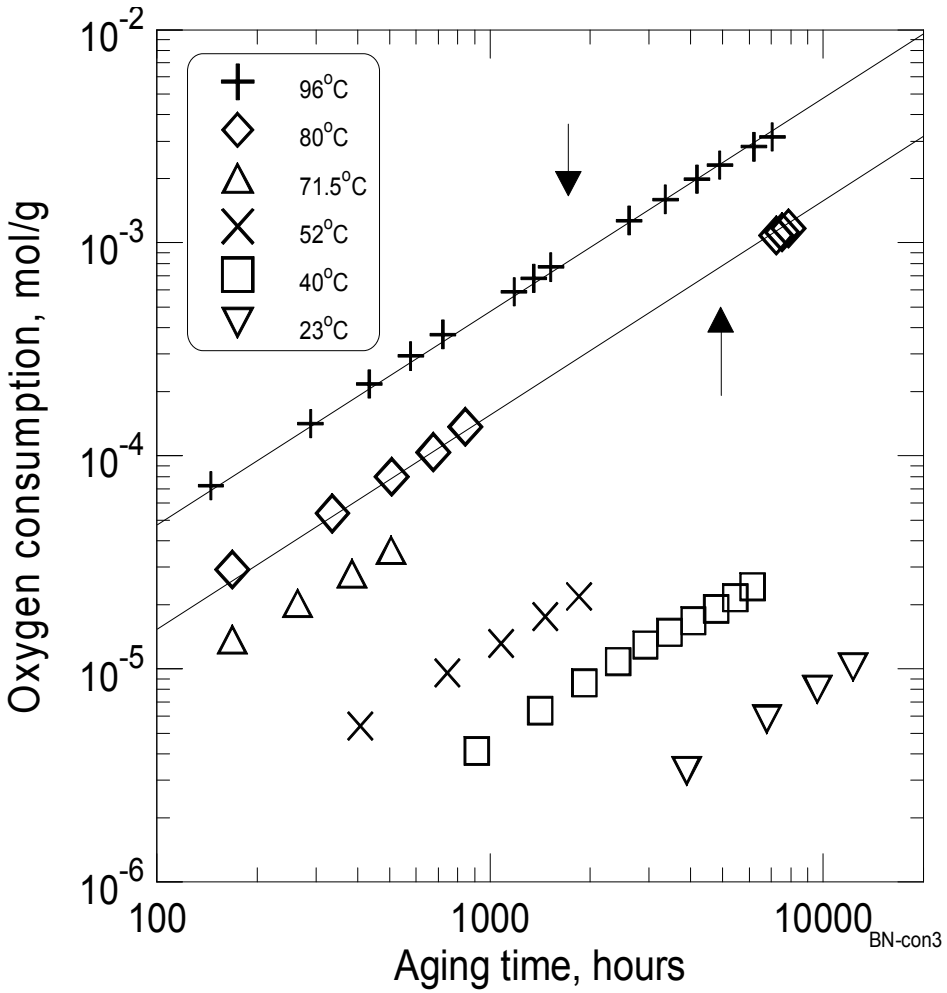
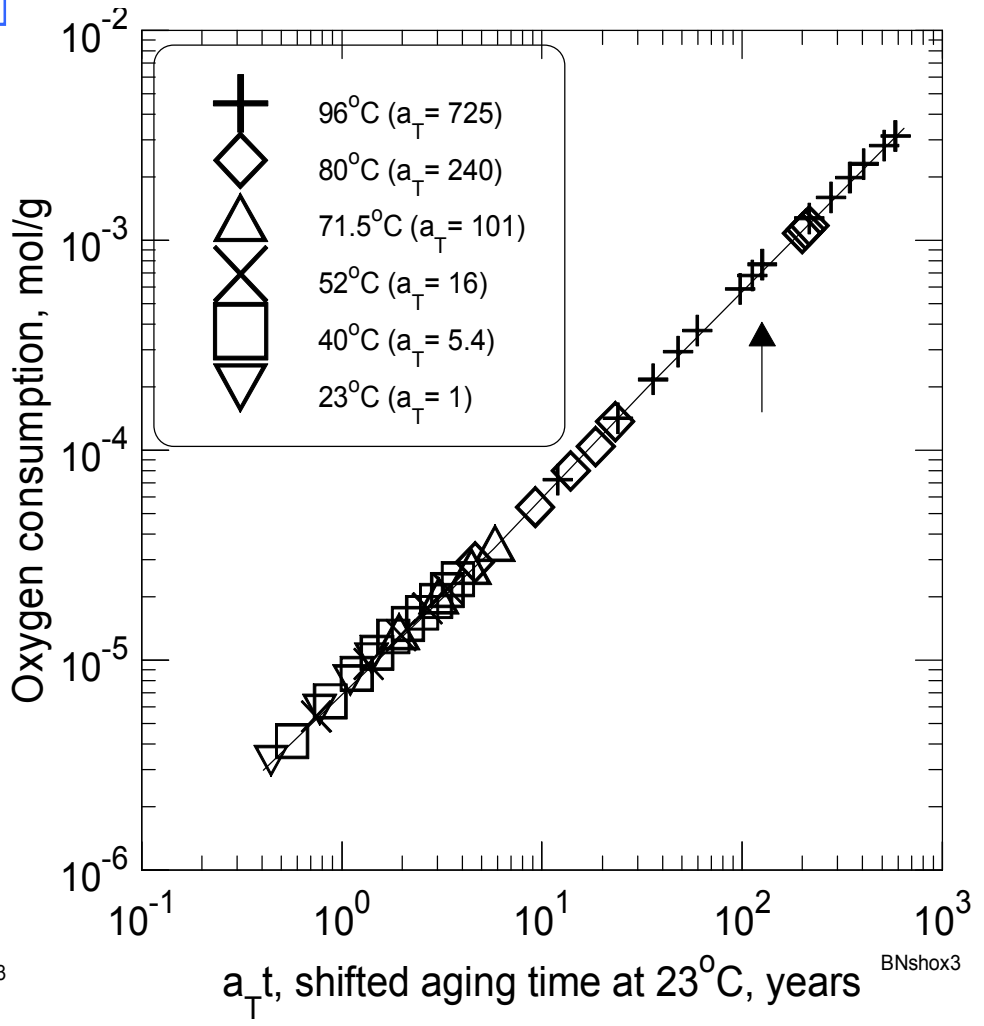
Integrated O_2 consumption



t-T superposition of integrated consumption



Arrows indicate where *e* reaches ~100%

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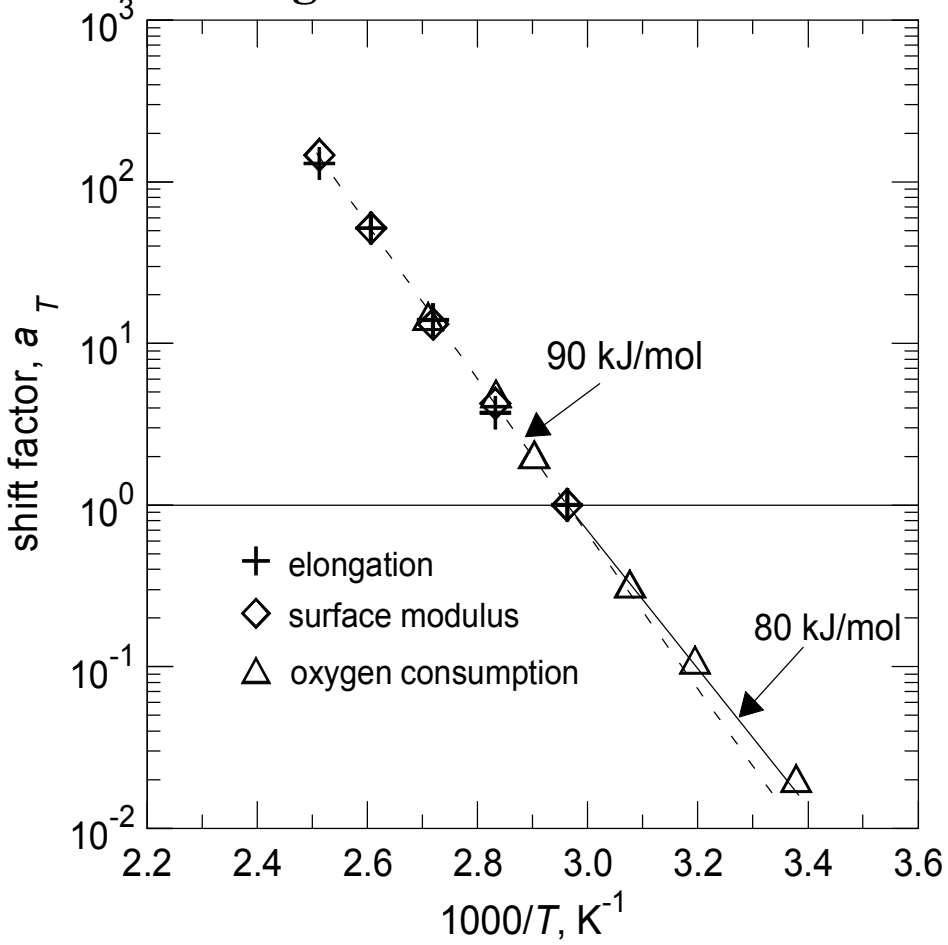
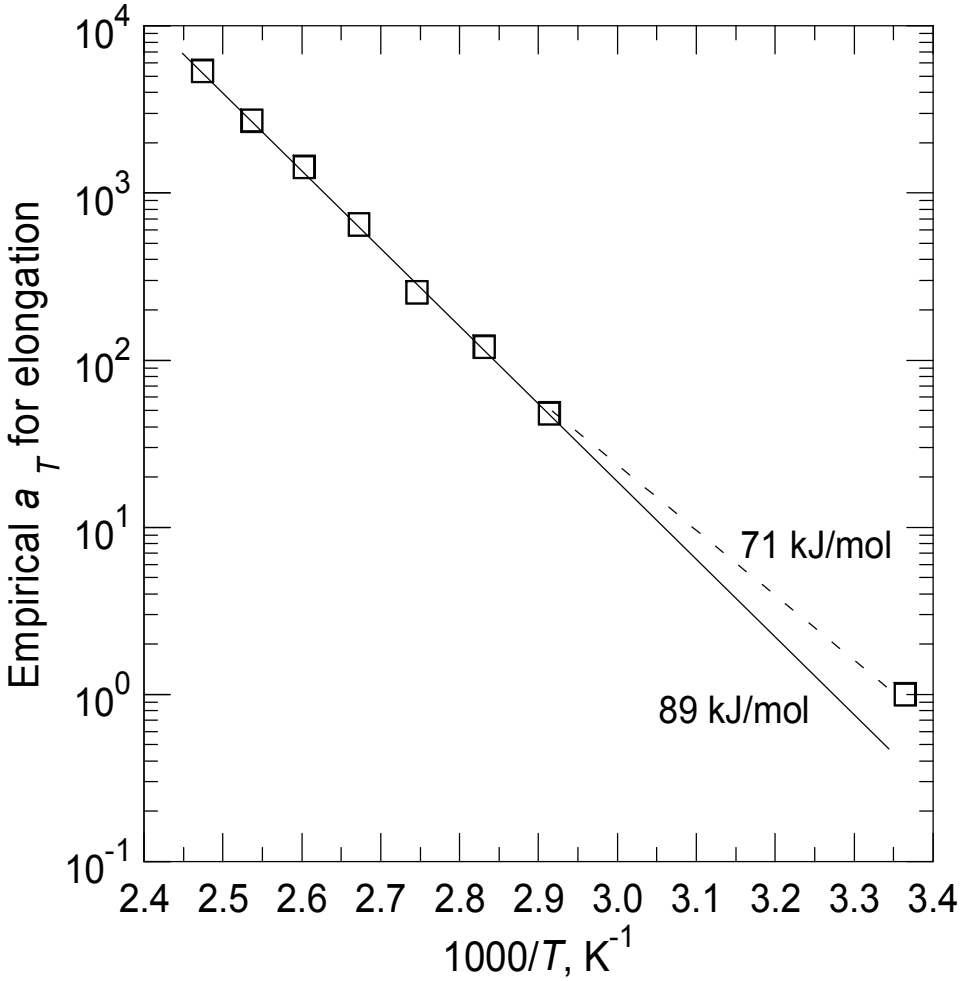
Compare a_T of *e*, surface modulus & *UOC*- slight curvature in Arrhenius



Earlier direct *e* to 25C of Okonite neoprene showed Arrhenius curvature



Same E_a in overlap region & *UOC* finds slight drop in E_a below 65°C

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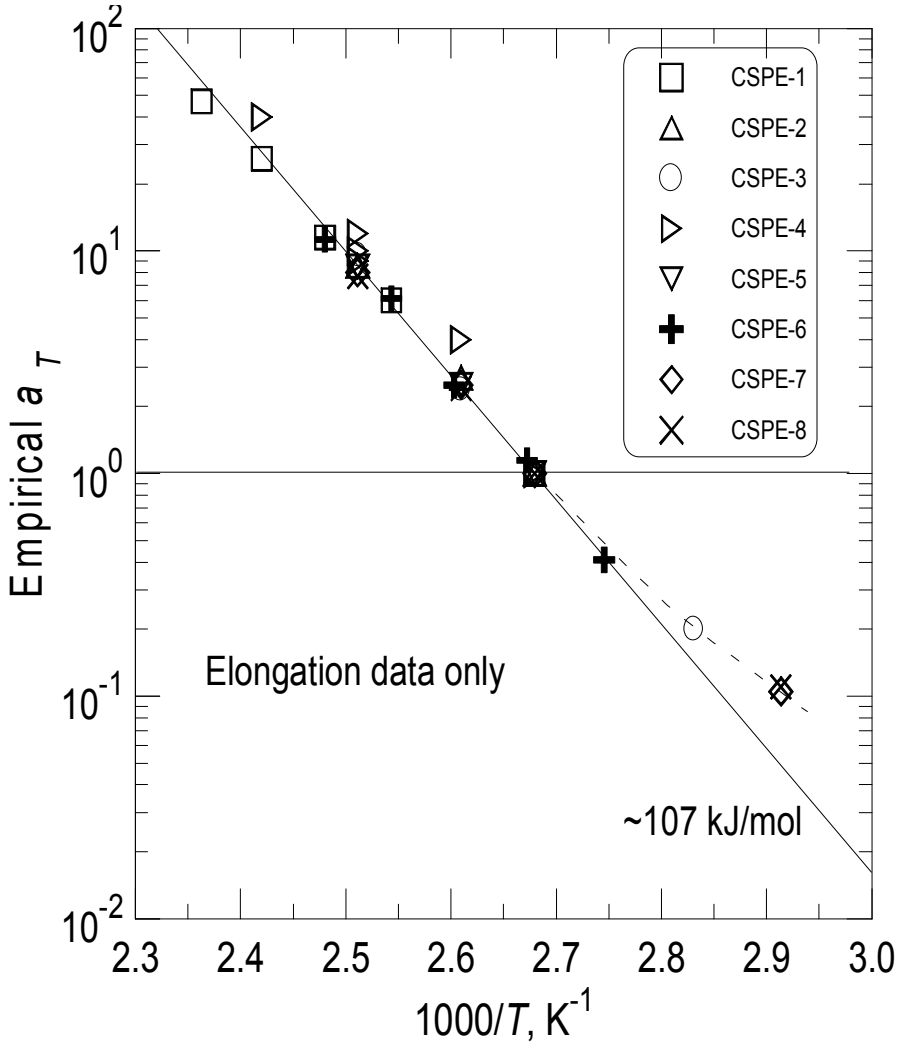
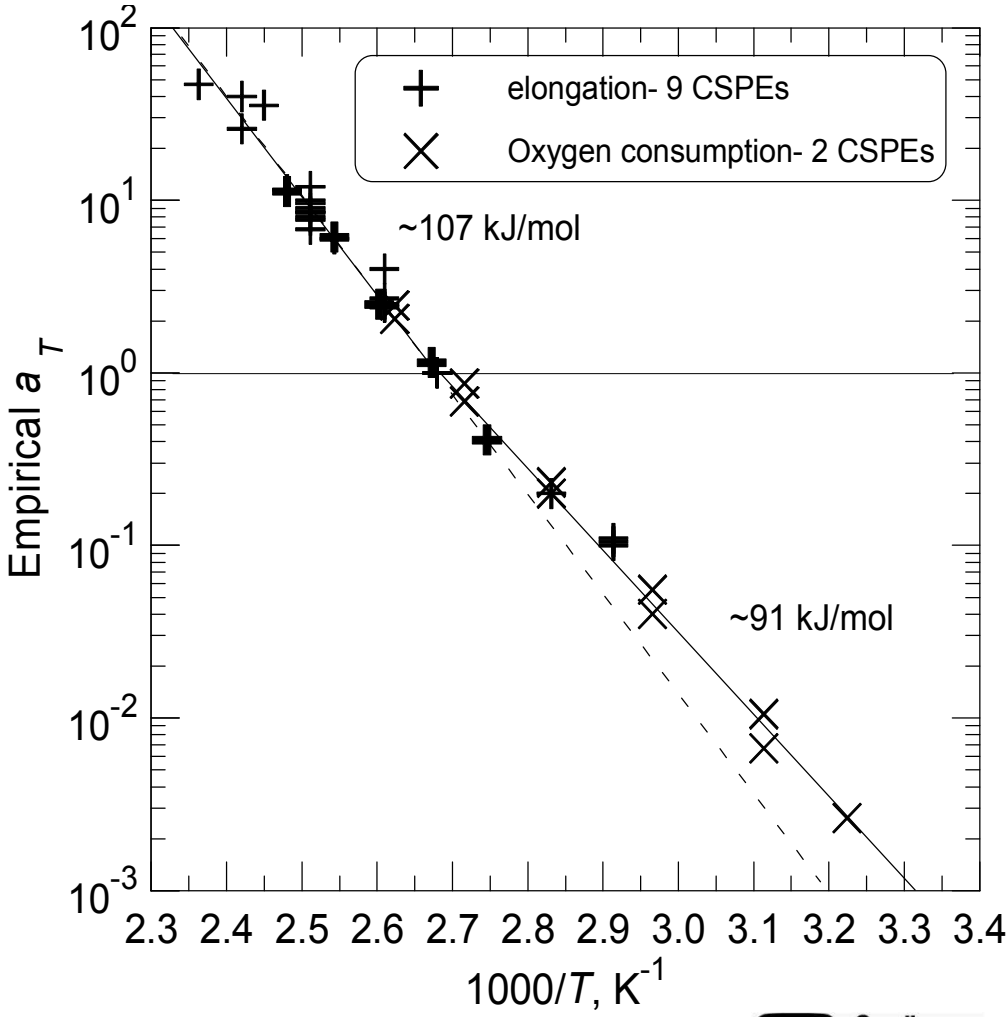
Eight different CSPE cable jackets

Elongation results down to ~70°C- curvature obvious at lower *T*s



Add ϕ results down to ~35°C- curvature from *e* confirmed



Ref- K. T. Gillen, R. Bernstein and M. Celina, Polym. Deg. & Stabil. 87, 335(2005).

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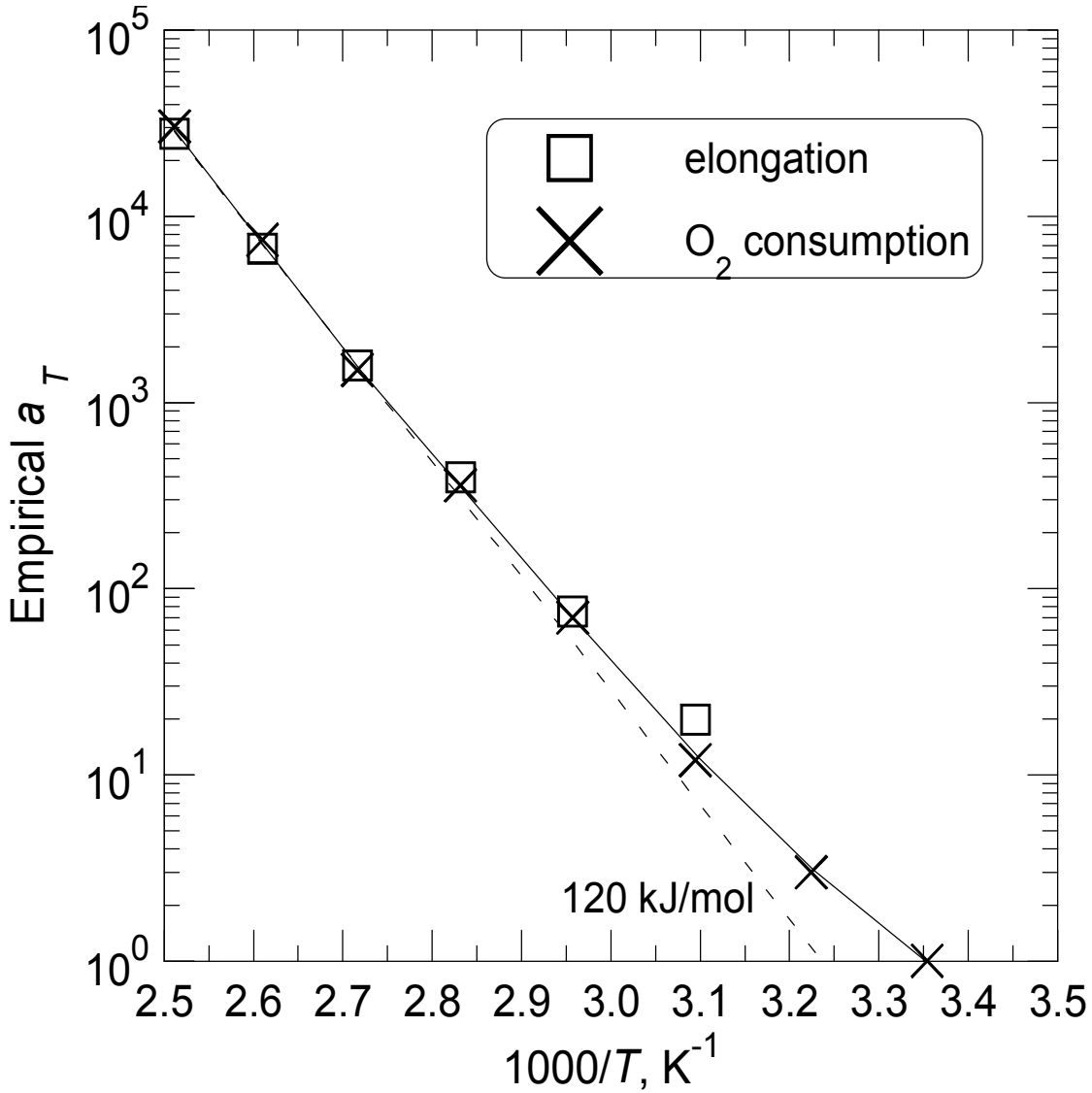
HTPB/IPDI based polyurethane rubber

Ref- M. Celina, et. al., Rubber Chem. Technol., 73, 678 (2000).



Non-Arrhenius for both ϕ and elongation results

Note- room temperature lifetimes reduced by ~85%

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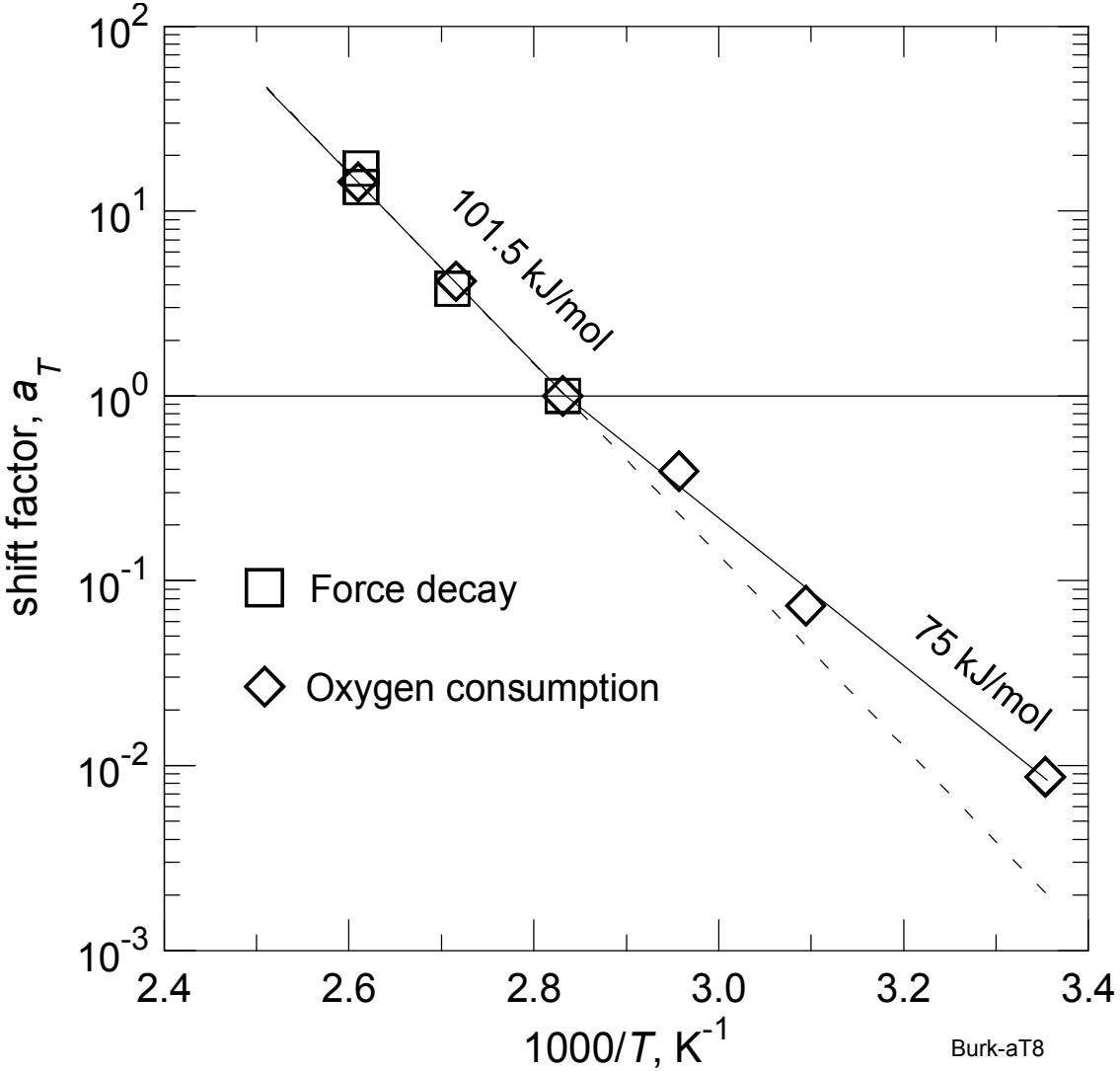
Burke butyl o-ring

Ref- K. T. Gillen, M. Celina & R. Bernstein, Polym. Degrad. Stabil., 82, 25 (2003)



Burk-aT8

ϕ agrees with elongation at high temperatures but indicates a change in E_a in extrapolation regime

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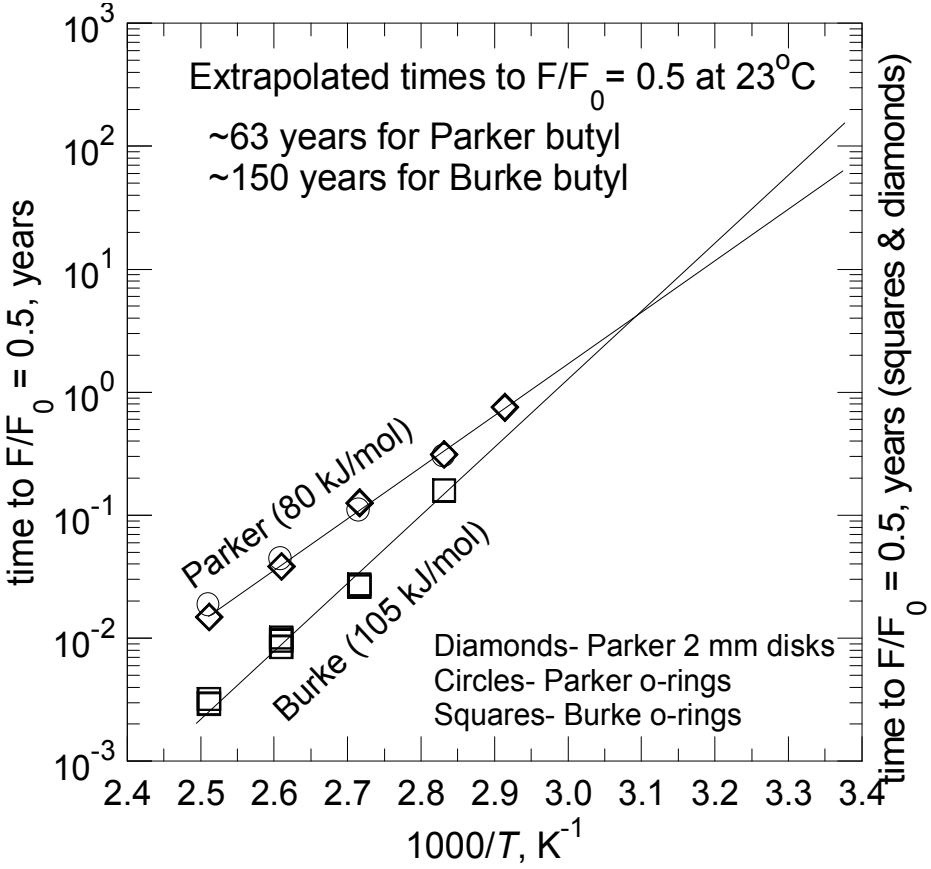
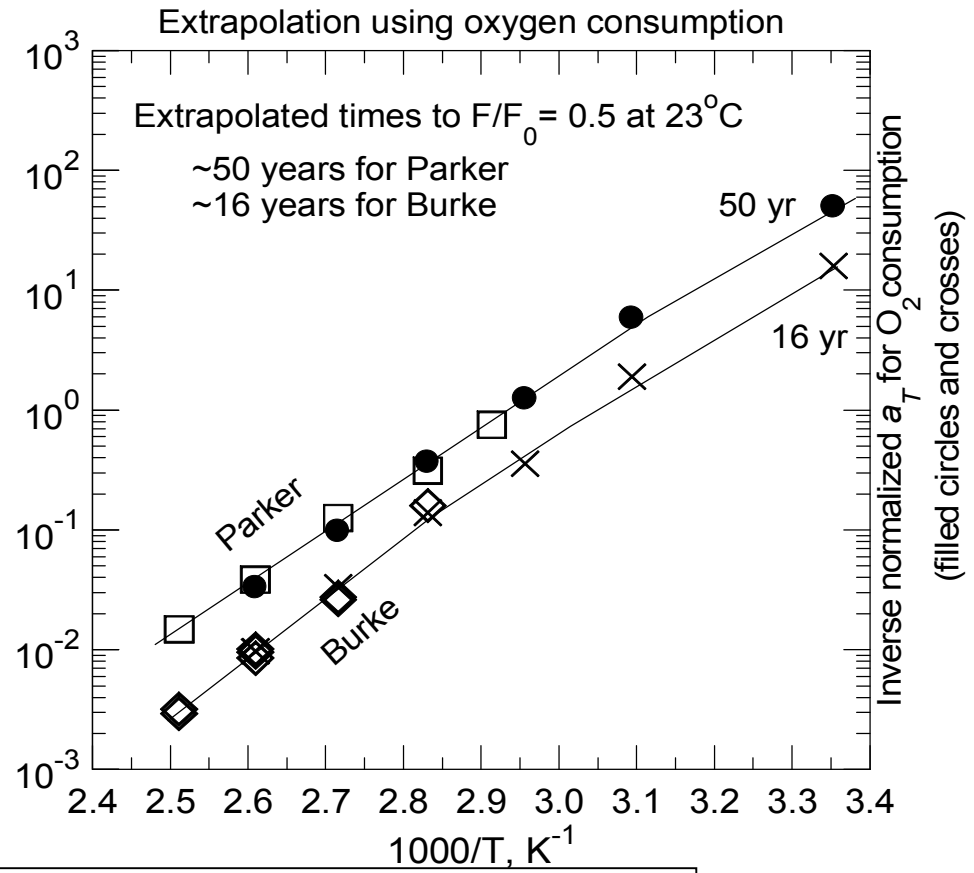
Classical extrapolation predicts that Burke has longer life than Parker

Novel ϕ approach- Burke predicted to require ~16 yr to reach 50% vs. ~50 years for Parker





16 to 22 year-old surveillance o-rings show that force loss is ~50% for Burke vs. 10%±10% for Parker. Curvature therefore confirmed.

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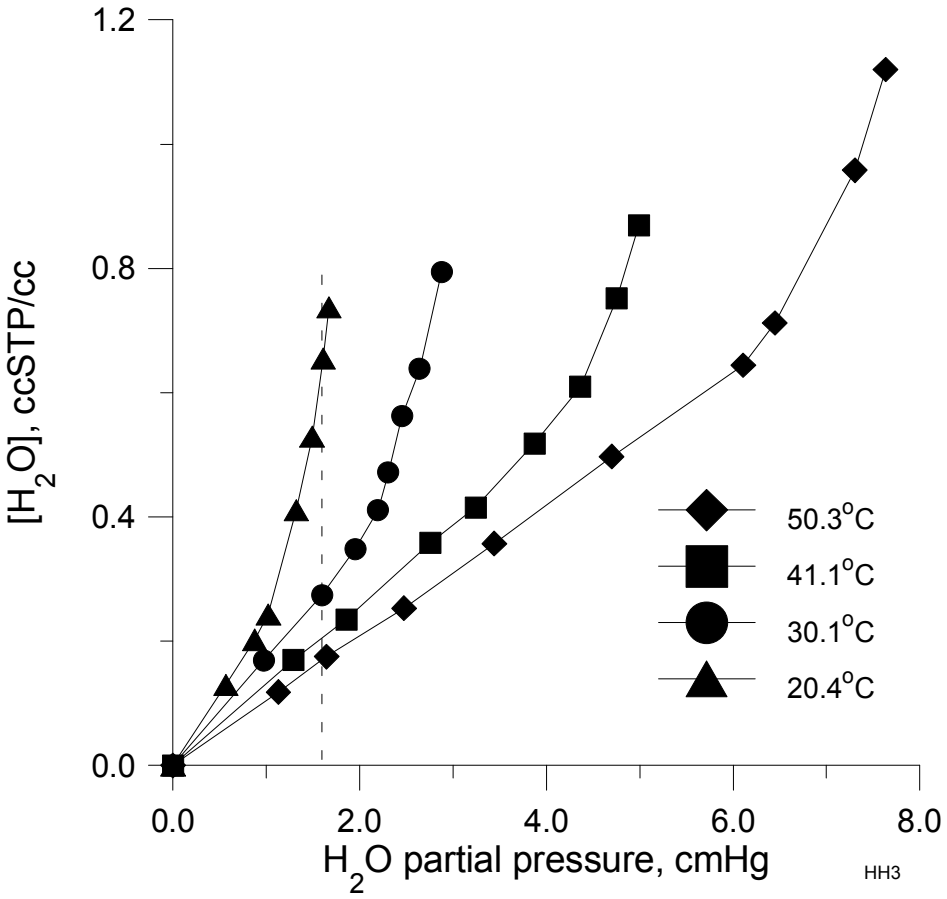
Conclusions for oxidation-dominated degradation

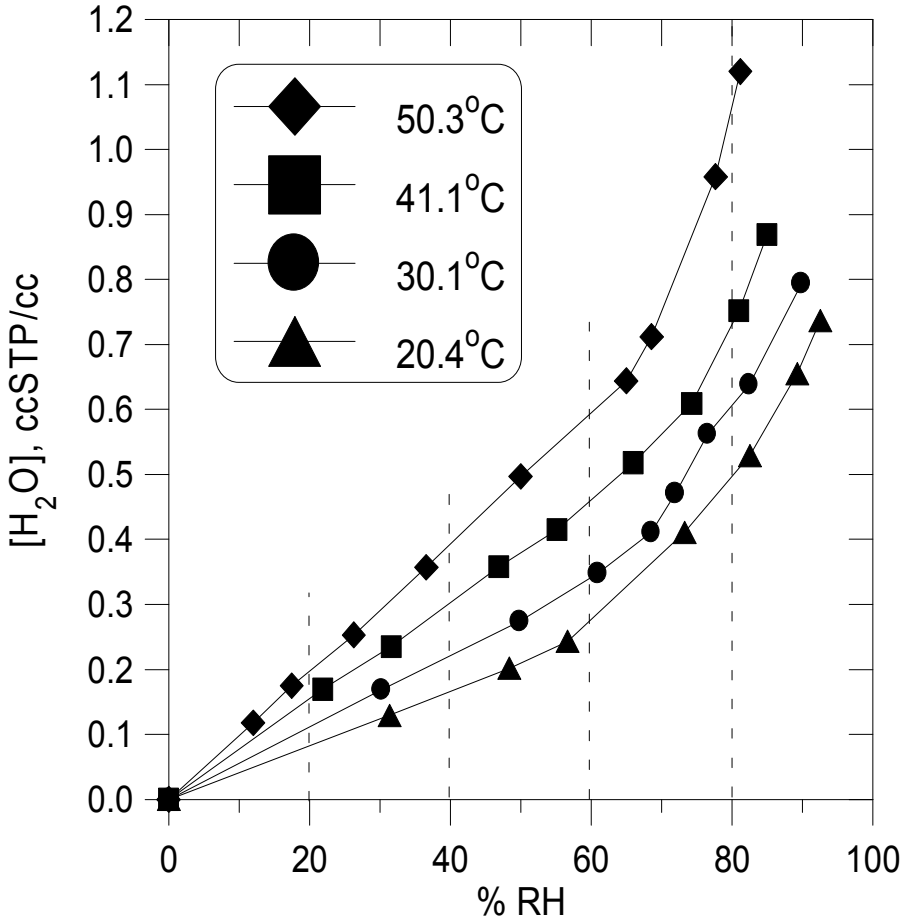
- *t-T* superposition is best analysis approach- checks equal acceleration assumption underlying accelerated aging
- ϕ measurements represent an excellent approach for testing Arrhenius extrapolations to temperatures lower than typical accelerated aging *T* range
- Results to date (both mechanical property and ϕ) indicate that curvature to lower E_a values is common
- This implies lower extrapolated polymer lifetimes
- Oxygen consumption measurements can also be useful for other oxygen-containing degradation environments- examples include
  - high-energy radiation
  - UV
  - dynamic mechanical straining

SOLUBILITY OF CONDENSABLE FLUIDS (H_2O)

H_2O isotherms- silicone rubber- complex shapes



Replot vs. RH



Analyze at various constant RHs using Arrhenius form

Ref- J. A Barrie & D. Machin, J Macromol. Sci. Phys. B3(4), 645 (1969).

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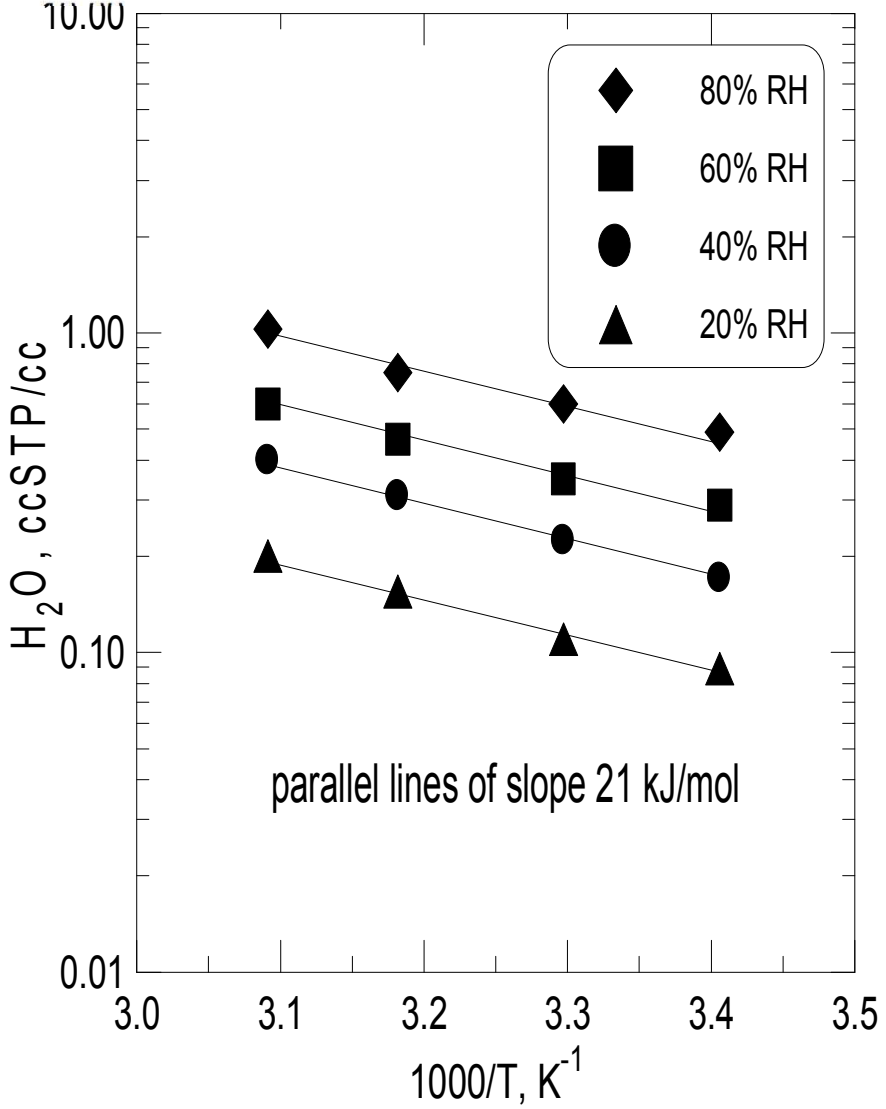
APPROACH FOR ANALYZING HUMIDITY AGING



- **Solubility at constant RH gives Arrhenius behavior independent of RH**
- **At each RH find that**

$$H_2O \sim \exp[-\Delta H_{RH}/RT]$$

- **Therefore carry out & analyze experiments at constant RH**

$$dD/dt = k[H_2O][P] \sim \exp[-\Delta H_{RH}/RT] \exp[-E_a/RT] \sim \exp[-E_a - \Delta H_{RH}/RT]$$

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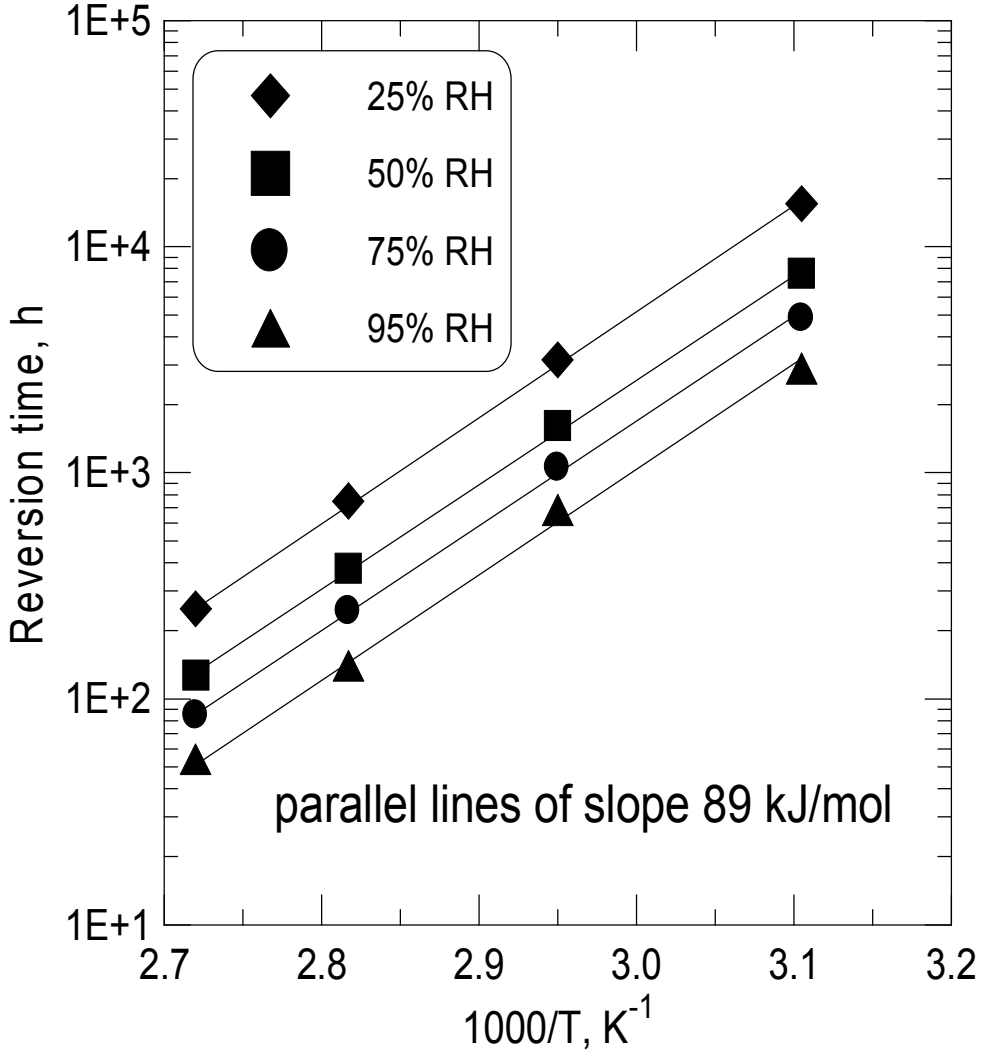
HUMIDITY AGING EXAMPLE

Ref- K. T. Gillen & K. E. Mead, SAND79-1561

Reversion of polyurethane potting compound- data from G. L. Welch, Natl. SAMPE Tech. Conf. Proc., Vol. 2 (1970)



- **Can extrapolate to lower *T***
- **Similar parallel Arrhenius lines at constant RH's noted for other materials, e.g.,**

Examples

Polyester- R. R. Dixon, Polym. Eng. Sci., 33, 65(1993)

Cellulose- X. Zou, et. al., Cellulose 3, 243(1996).

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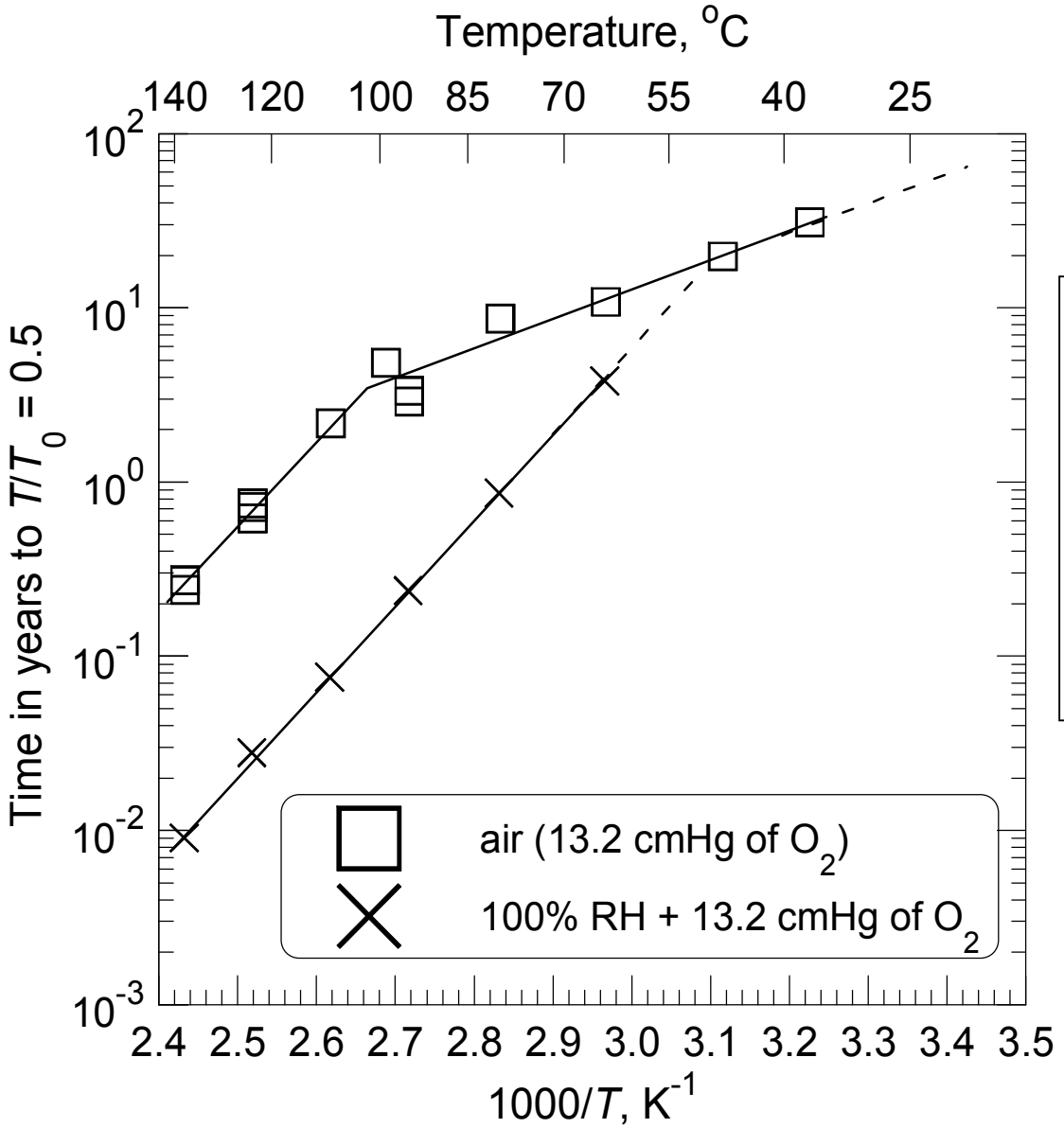
Interesting example- Nylon 6,6 aged versus *T* at 100% RH

Ref- R. Bernstein & K. T. Gillen, Polym. Degrad.& Stabil., 95, 1471(2010).



Interesting example since higher E_a humidity results must transition to lower E_a air aging results below ~50°C (e.g., lower E_a chemistry takes over at lower temperatures)

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