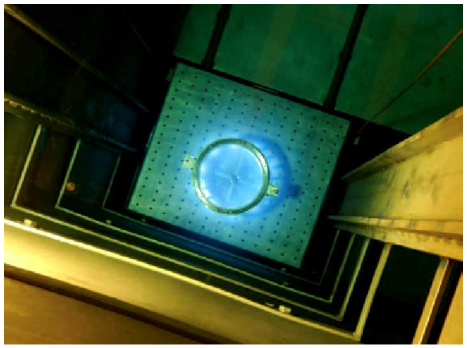
SAND2013-2189P

Exceptional service in the national interest

Sandia National Laboratories


Organic Material Aging and Degradation

Gregory Von White II, John L. Schroeder,

Patricia S. Sawyer, Derek J. Wichhart, Amy Garner,
Guillermo A. Mata, and Robert Bernstein

NRC Telecon Presentation - March 19, 2013

U.S. DEPARTMENT OF ENERGY | NNSA

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Collaborators

Sandia National Laboratories

AWE

U.S.NRC

OAK RIDGE National Laboratory

LWRS Light Water Reactor Sustainability

Los Alamos NATIONAL LABORATORY

Pacific Northwest NATIONAL LABORATORY

CNEA

Lawrence Livermore National Laboratory

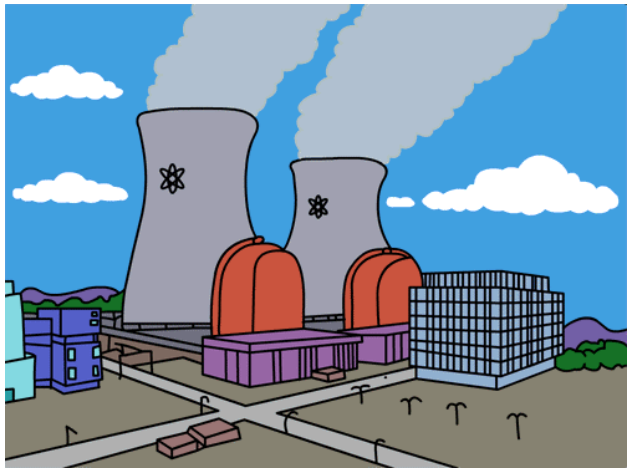
National Defence / Défense nationale

EPRI ELECTRIC POWER RESEARCH INSTITUTE

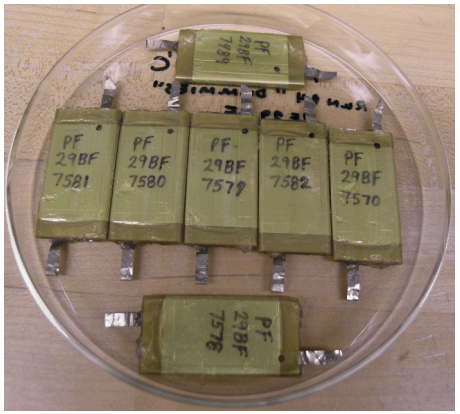
Organic Materials Employed in Service for Decades in Critical High Reliability and Performance Applications

Sandia National Laboratories

O-rings



Nuclear Power Plant Cable Insulation



Capacitors

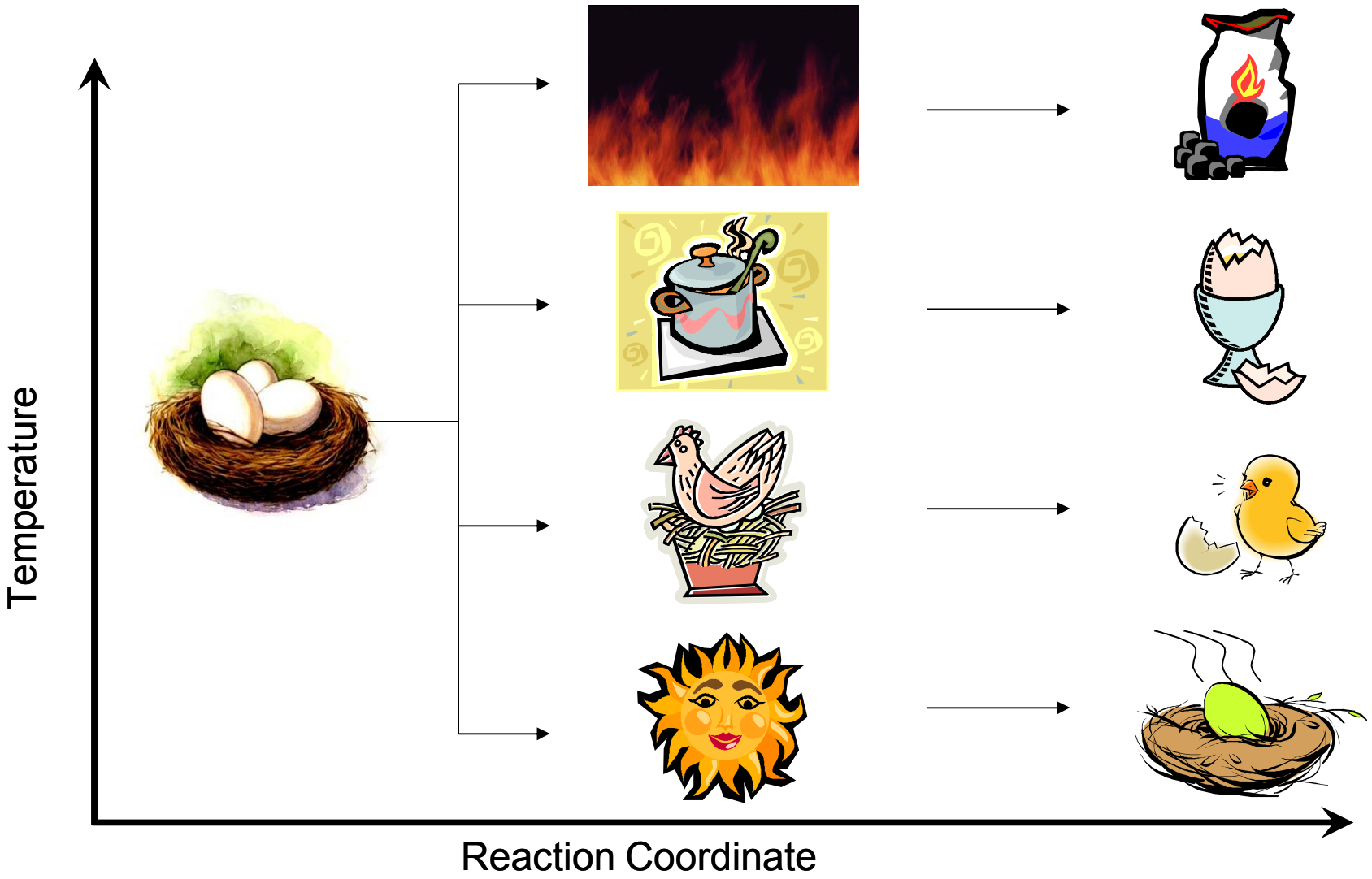
Textiles/Fibers

Glass Fiber Reinforced Epoxies

How do we accelerate time?

None of these are available or approved through **SNL suppliers**!

How do we accelerate time?



Polymer Aging - Approaches/Goals

Sandia National Laboratories

Macroscopic level

Physical Properties

Tensile Property

Flexural Strength

Compression Set

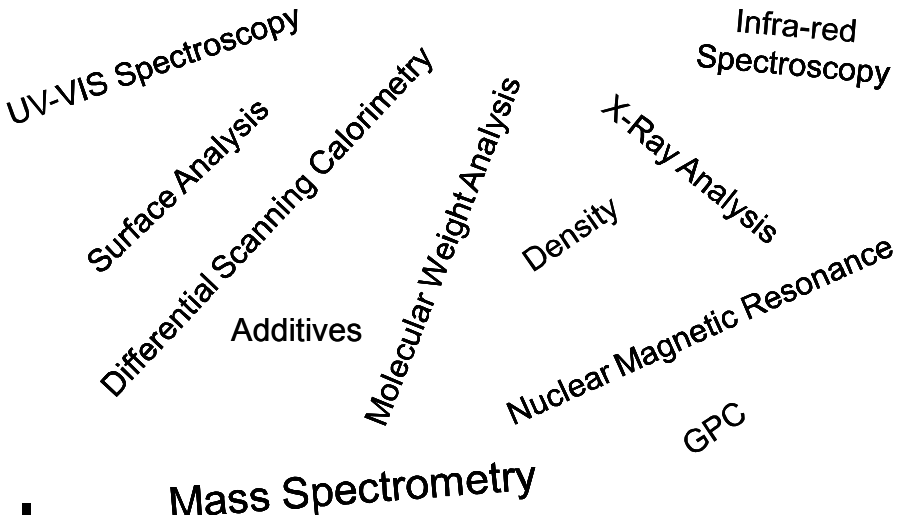
Permeation

Elongation

Dimensional changes

Molecular Level

Chemical Properties



Goals

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

Polymer Aging - Approaches/Goals

Sandia National Laboratories

Macroscopic level

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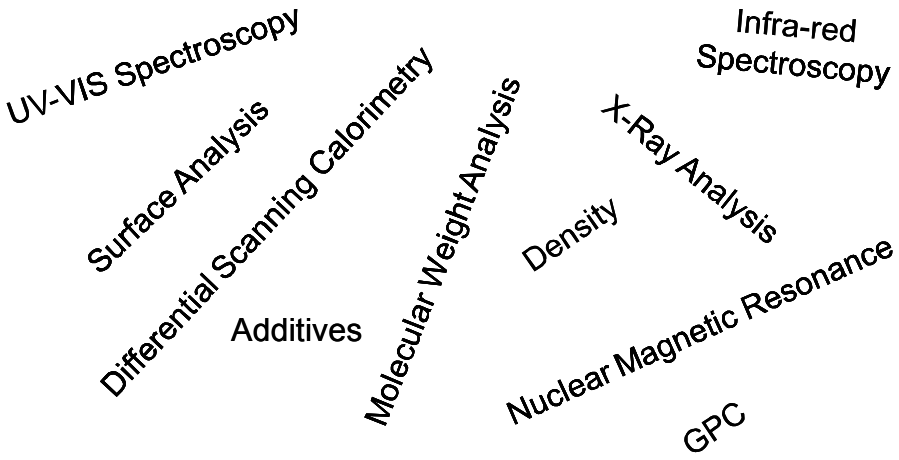
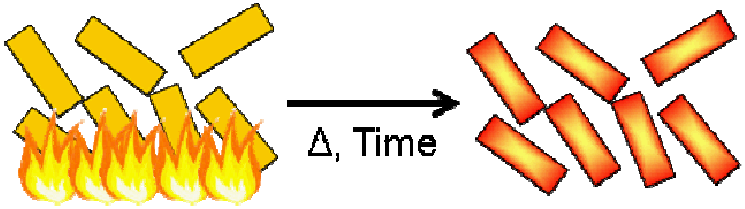


Goals

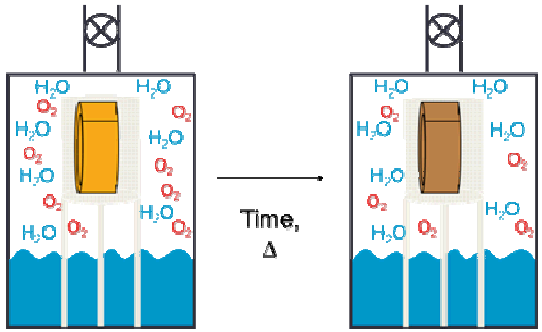
- **Prediction of physical properties vs. time**
  - **Predict remaining physical properties of field materials**
- Develop condition monitoring method

Applied Approach for Organic Materials



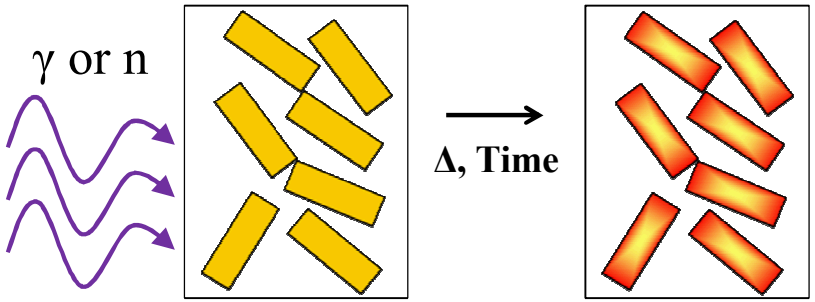
Thermal-Oxidative Aging

Increase Temperature



Humidity Aging

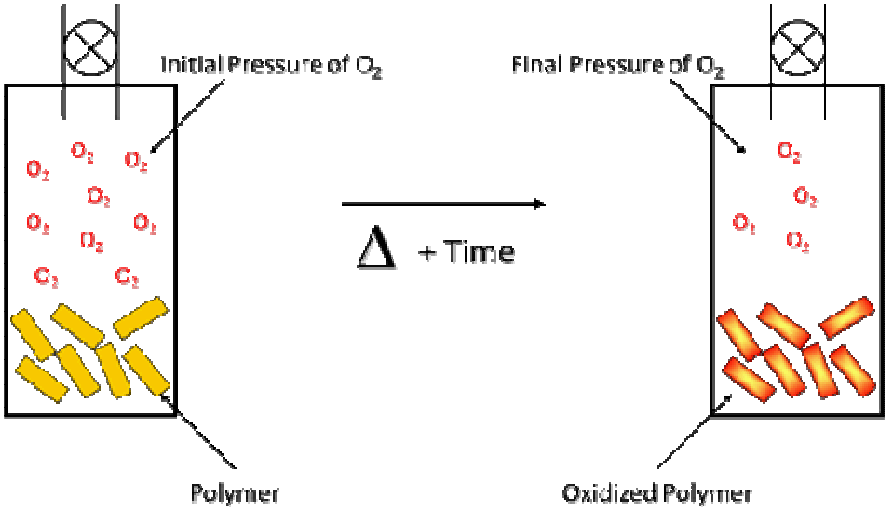
Increase Humidity



Radiation Aging

Increase Flux or Dose Rate

Fundamental Approach for Organic Materials



Oxygen Consumption

Mechanistic Studies

Sandia National Laboratories

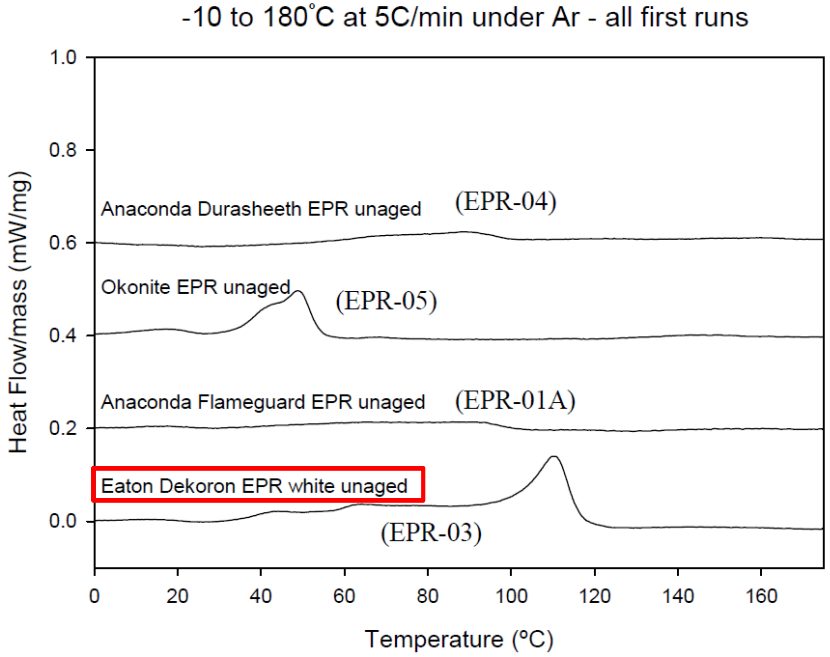
Model Development

NUCLEAR POWER PLANT CABLES

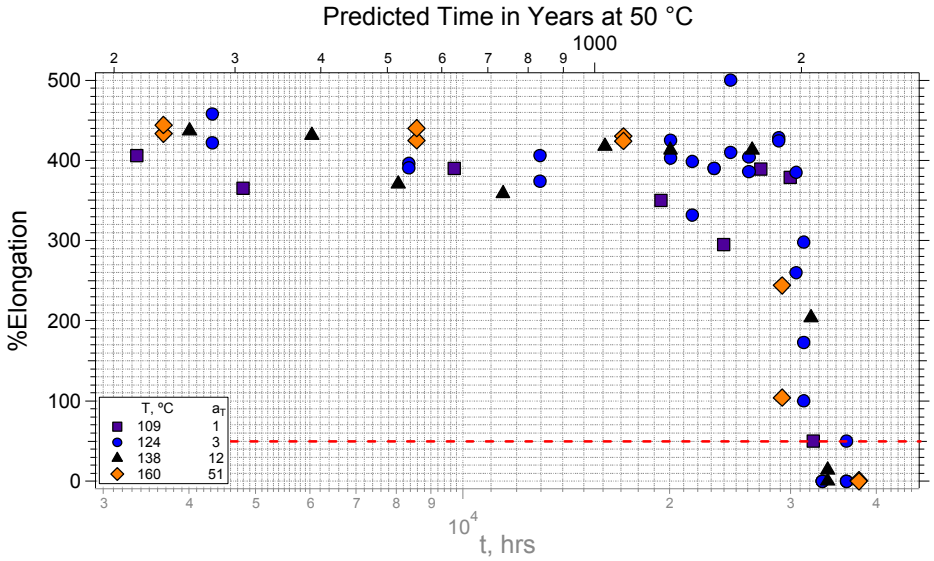
Ethylene Propylene Rubber (EPR)

Eaton Dekoron Elastoset EPR Cable Insulation

Highly crystalline polymer

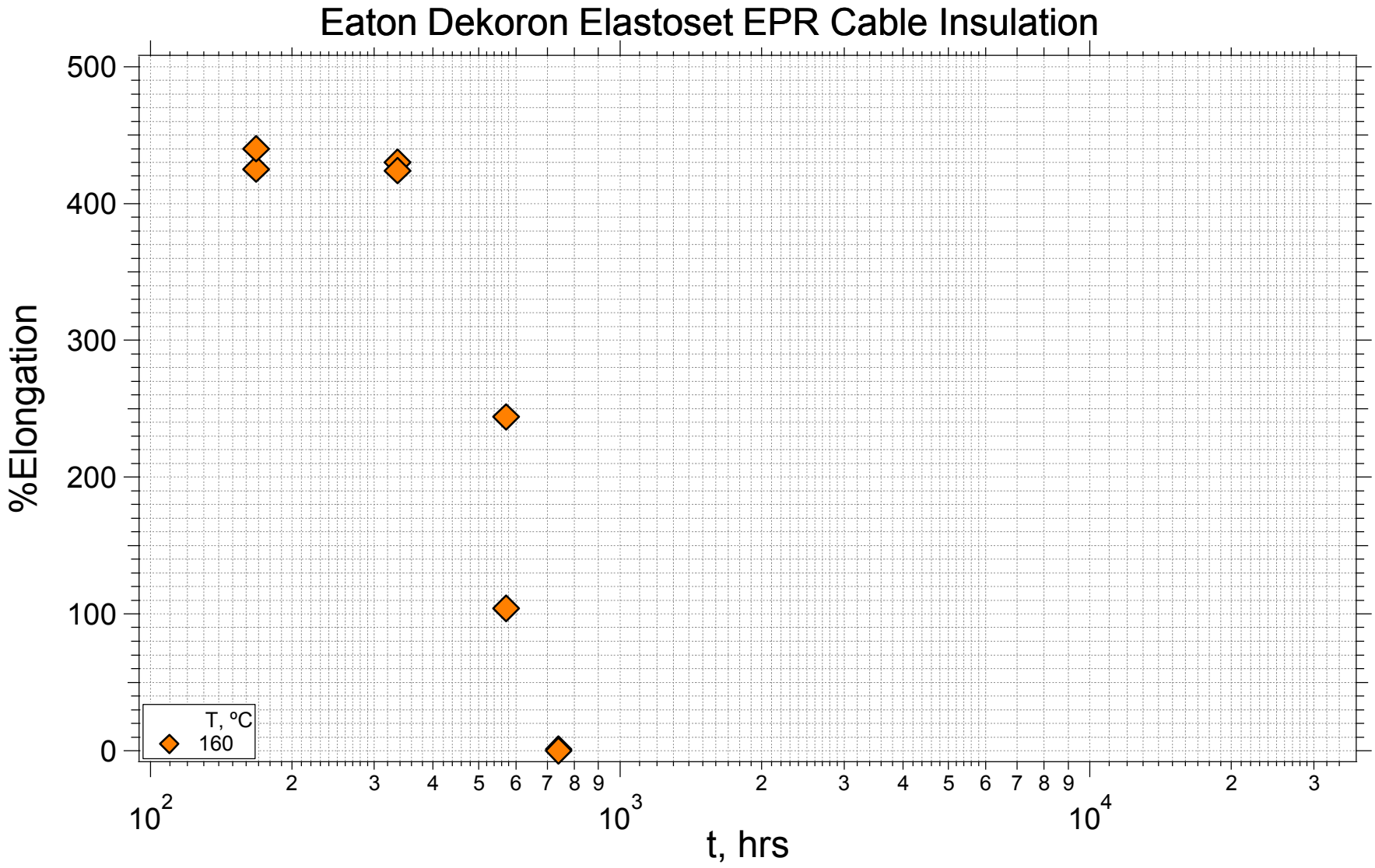


Exhibits Large "Induction Time"



SAND2005-7331 K. T. Gillen, R. A. Assink, and R. Bernstein

Tensile Properties – Thermal Aging



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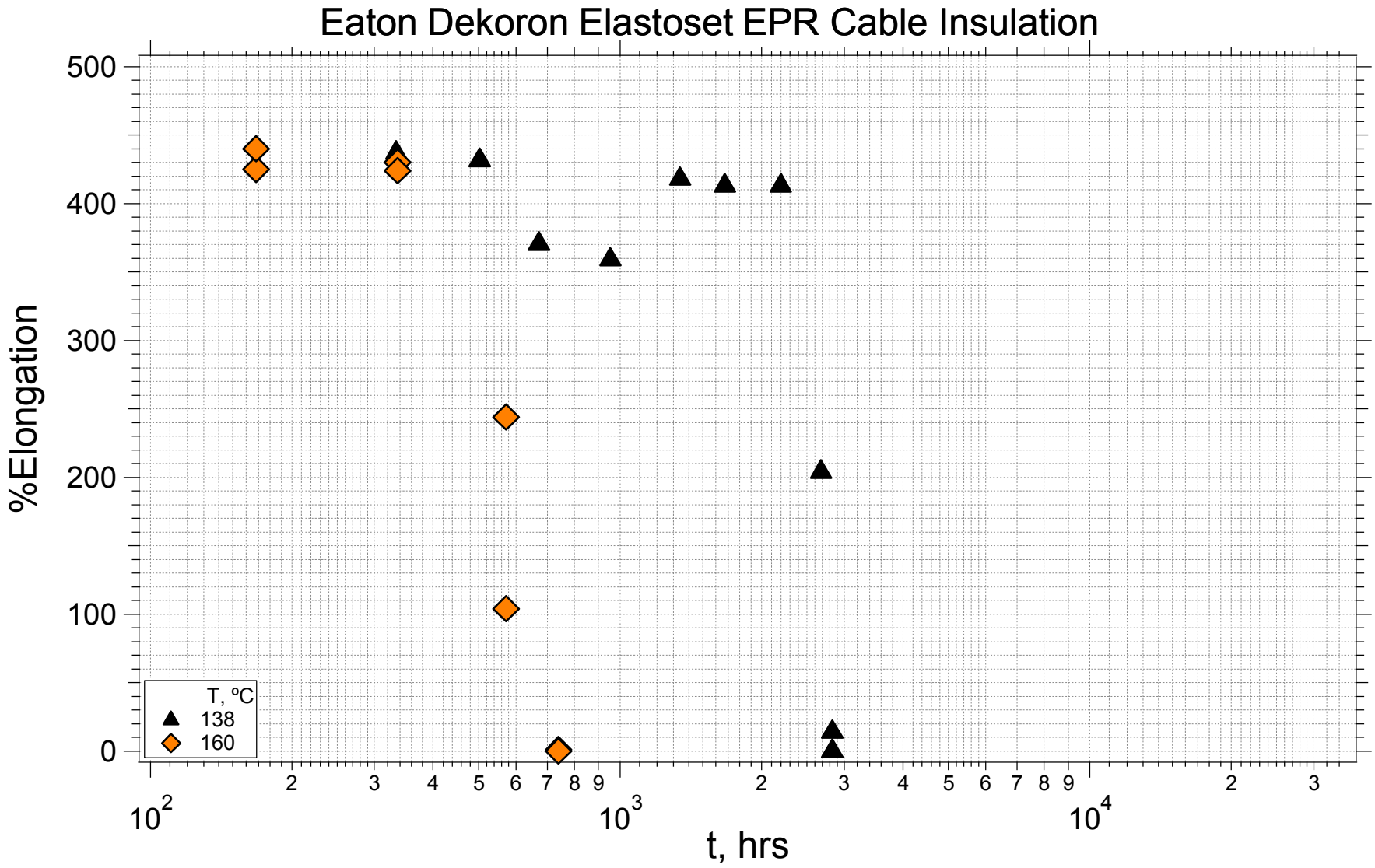

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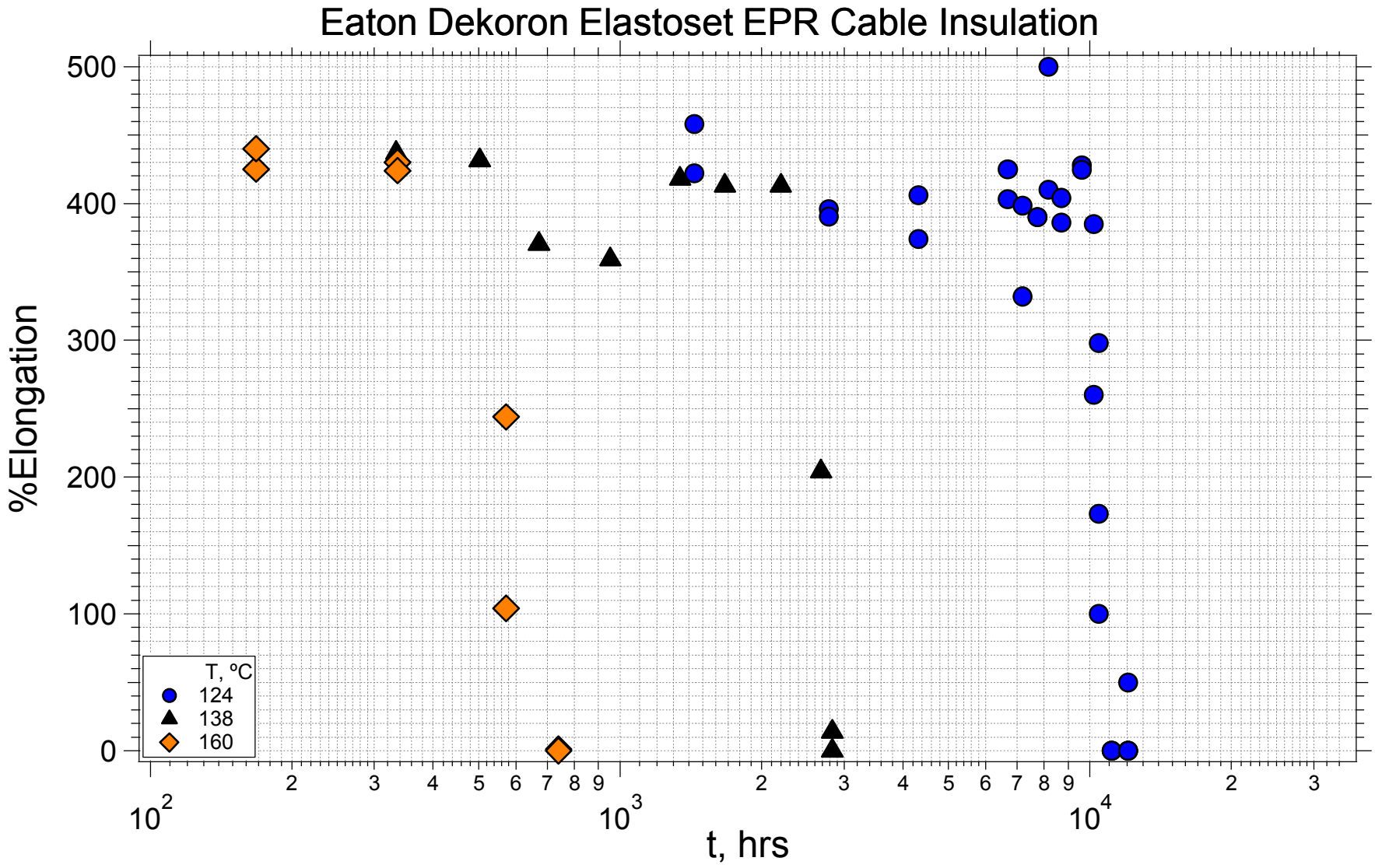

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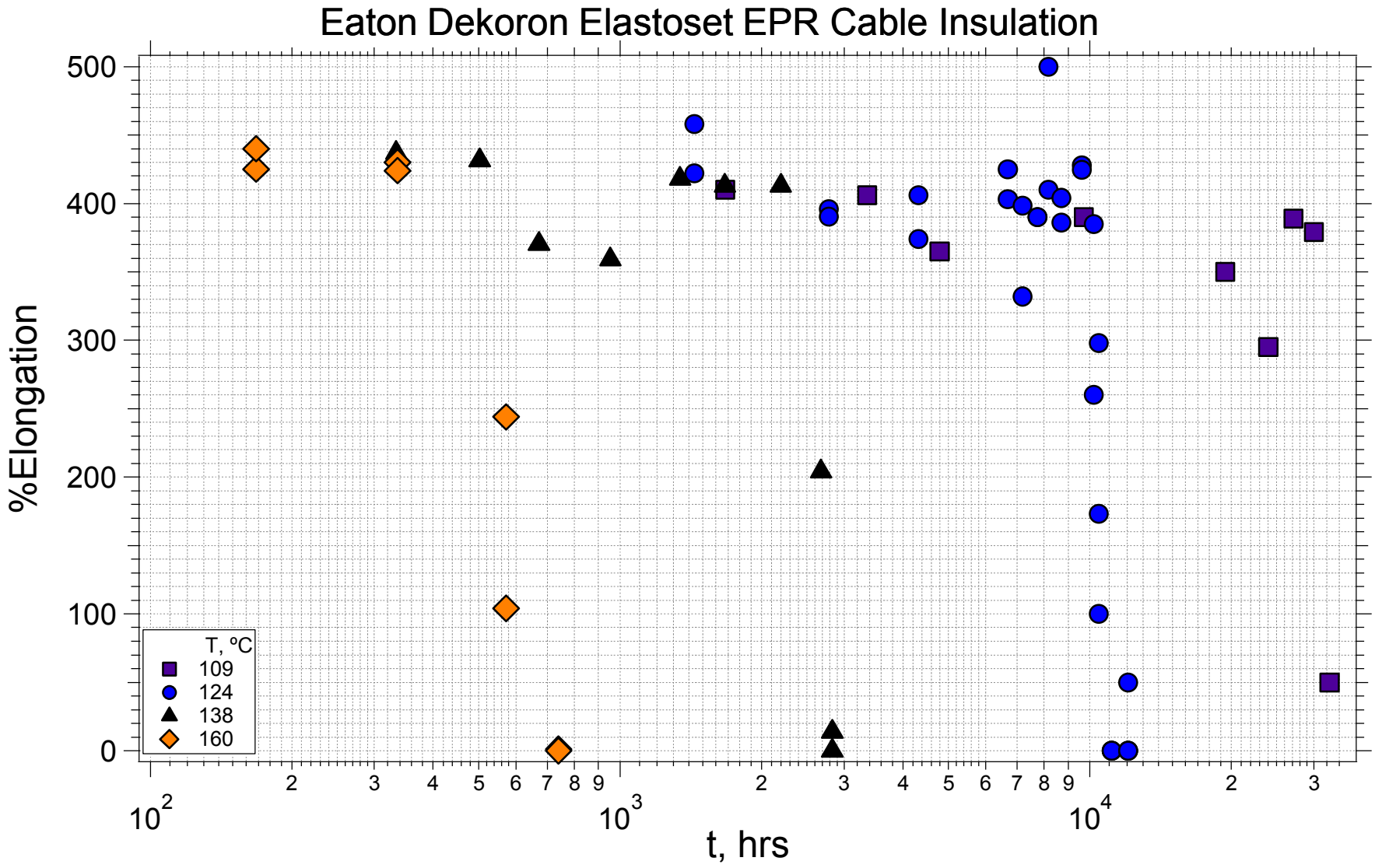

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Time-Temperature Superposition

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
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.

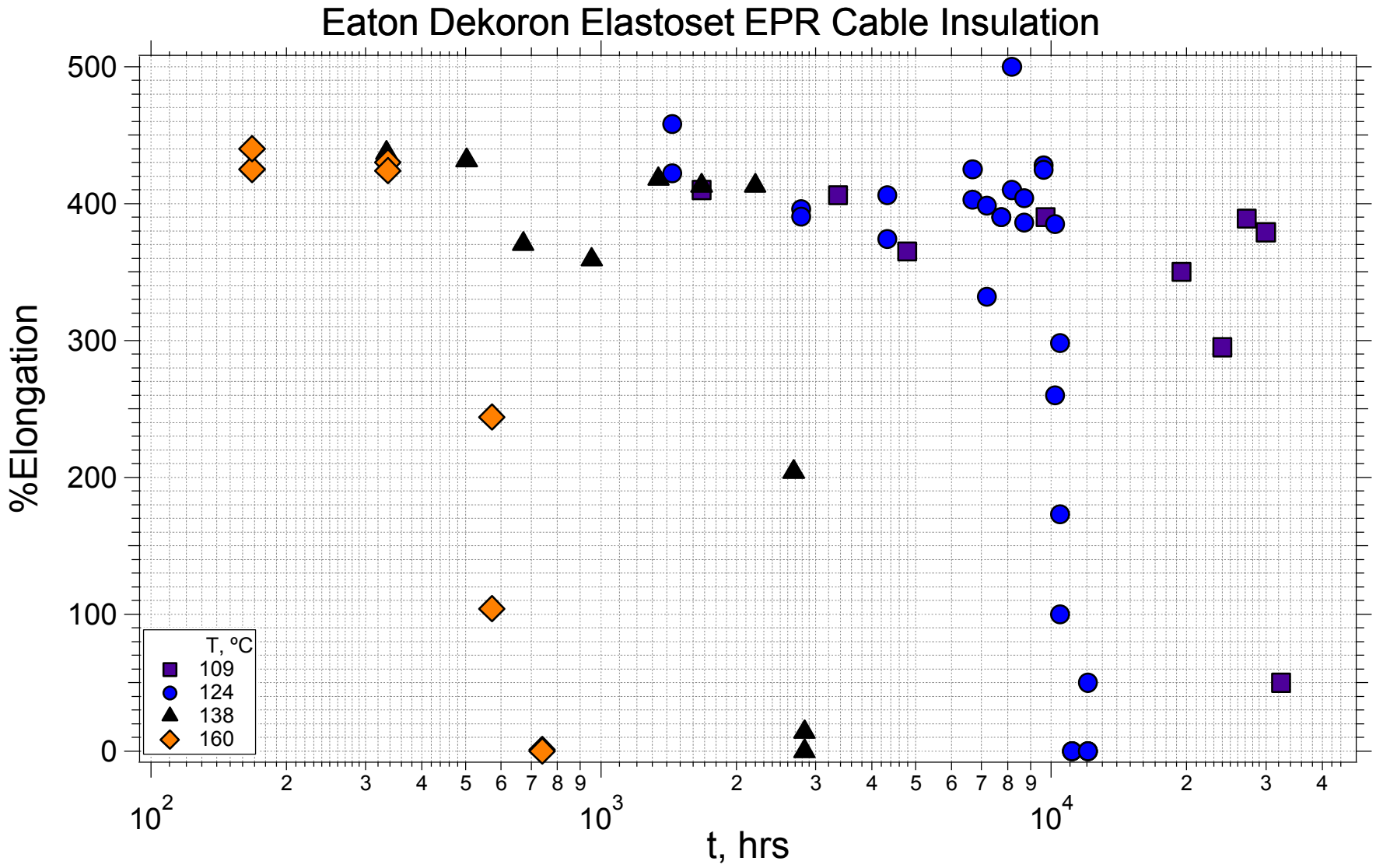
Arrhenius equation:

Empirical equation

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

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

Time-Temperature Superposition



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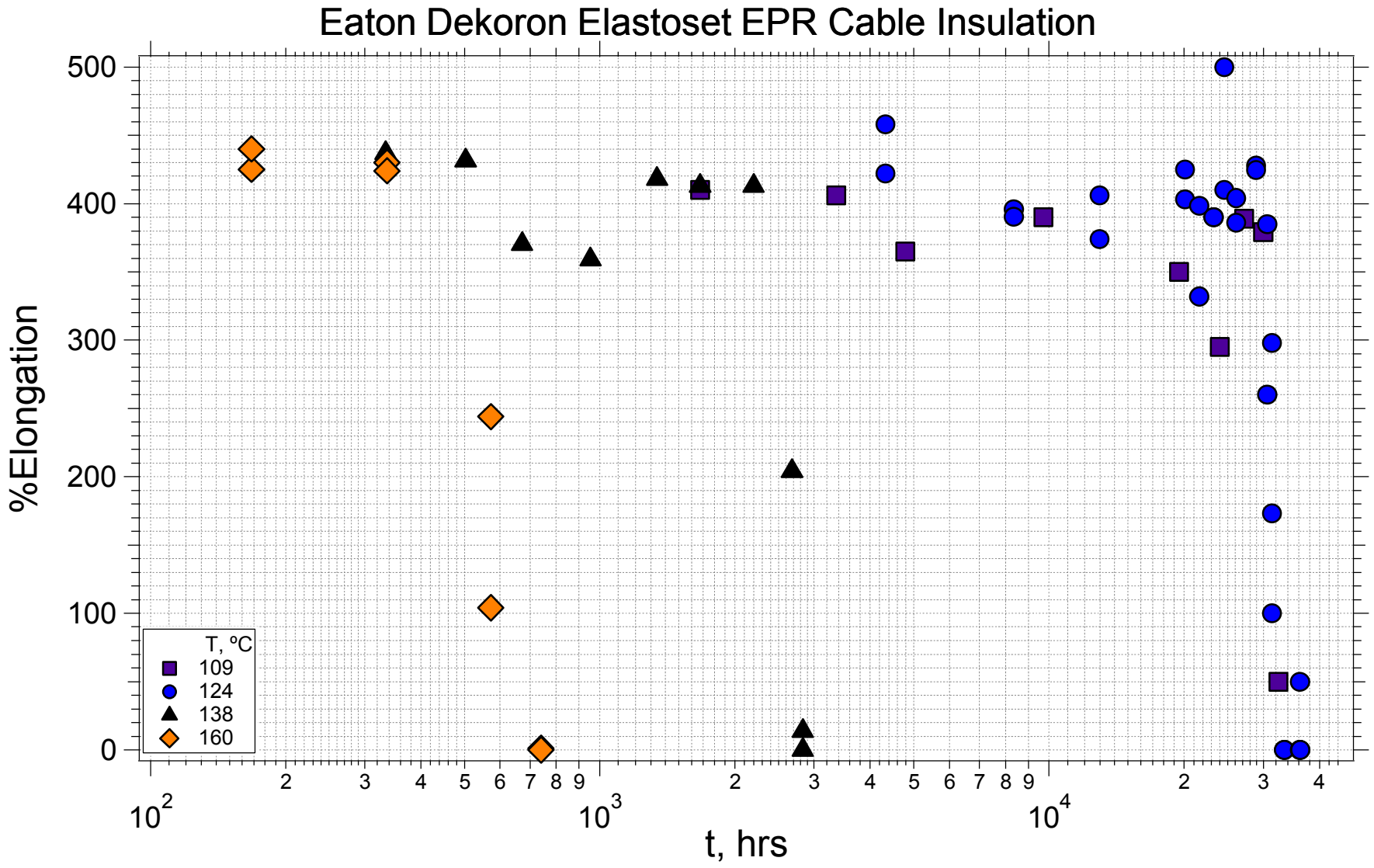

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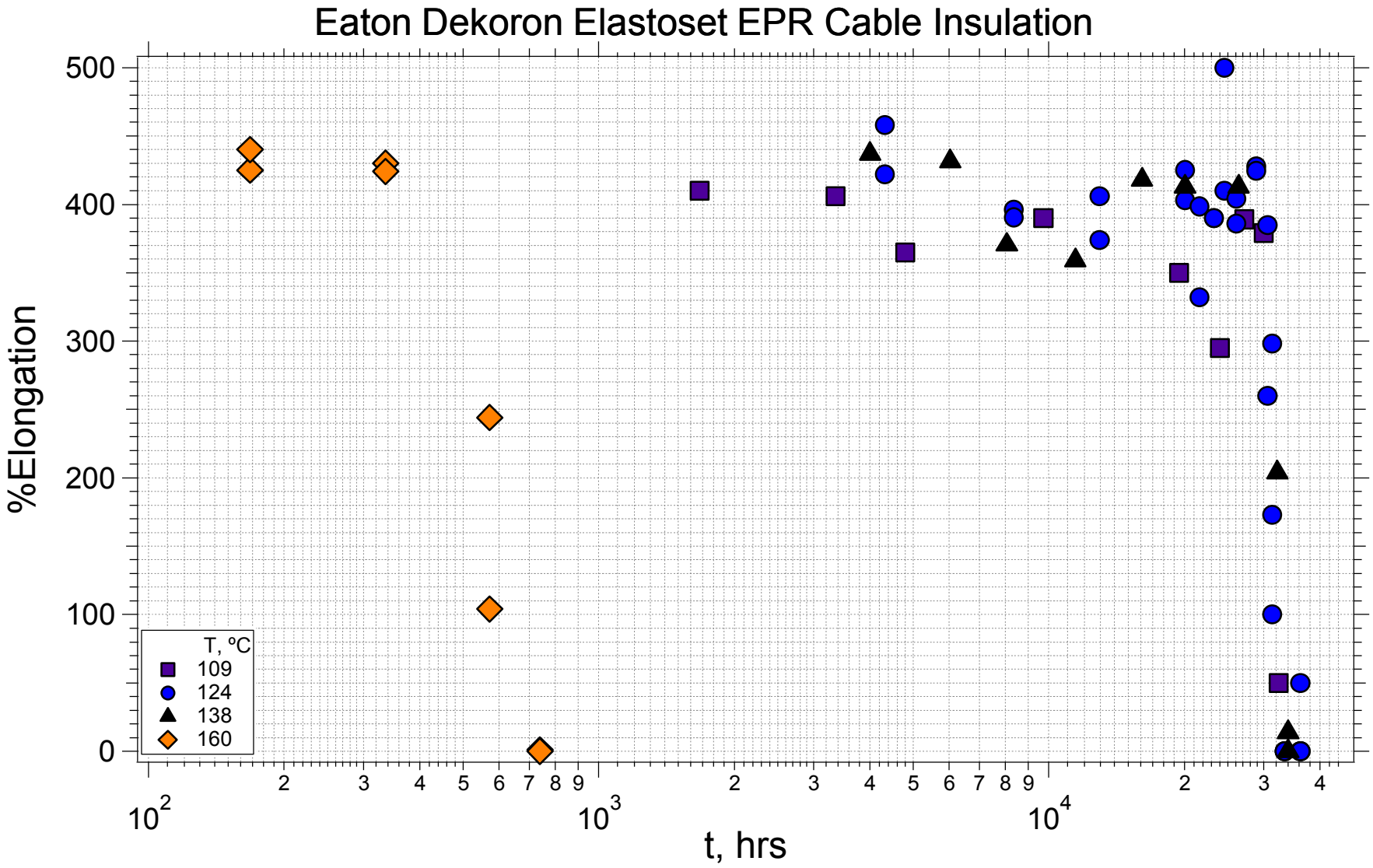

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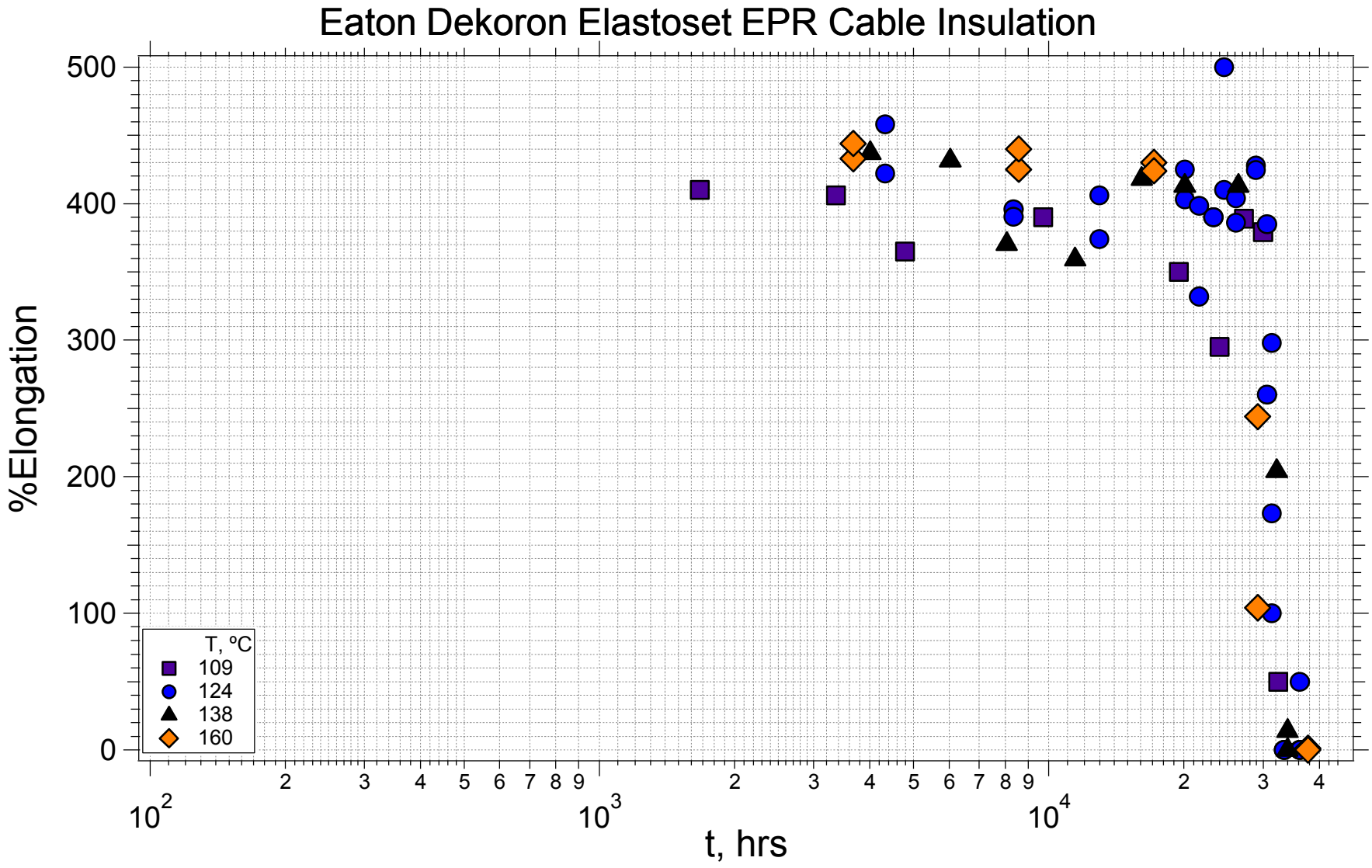

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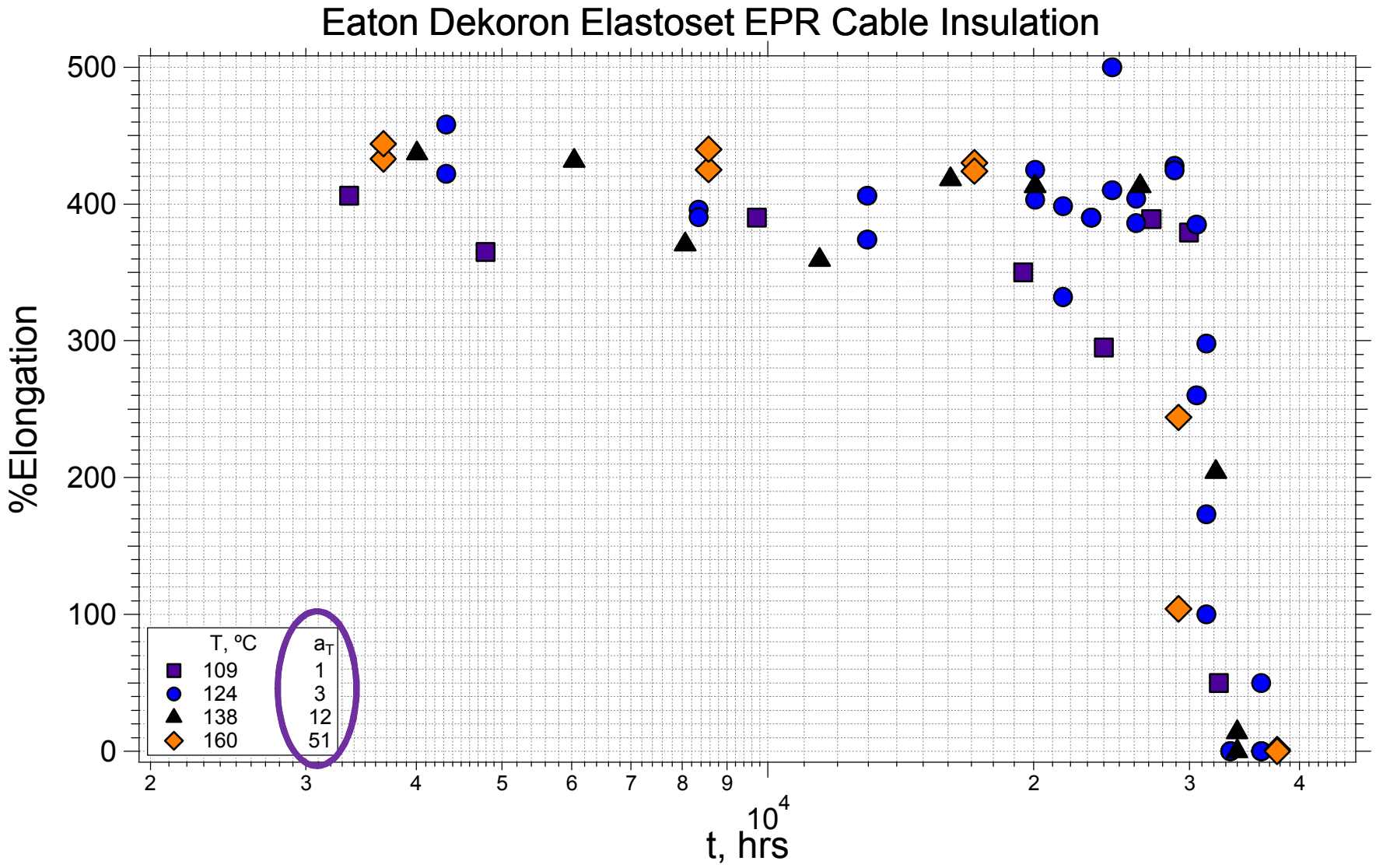
Arrhenius Plot



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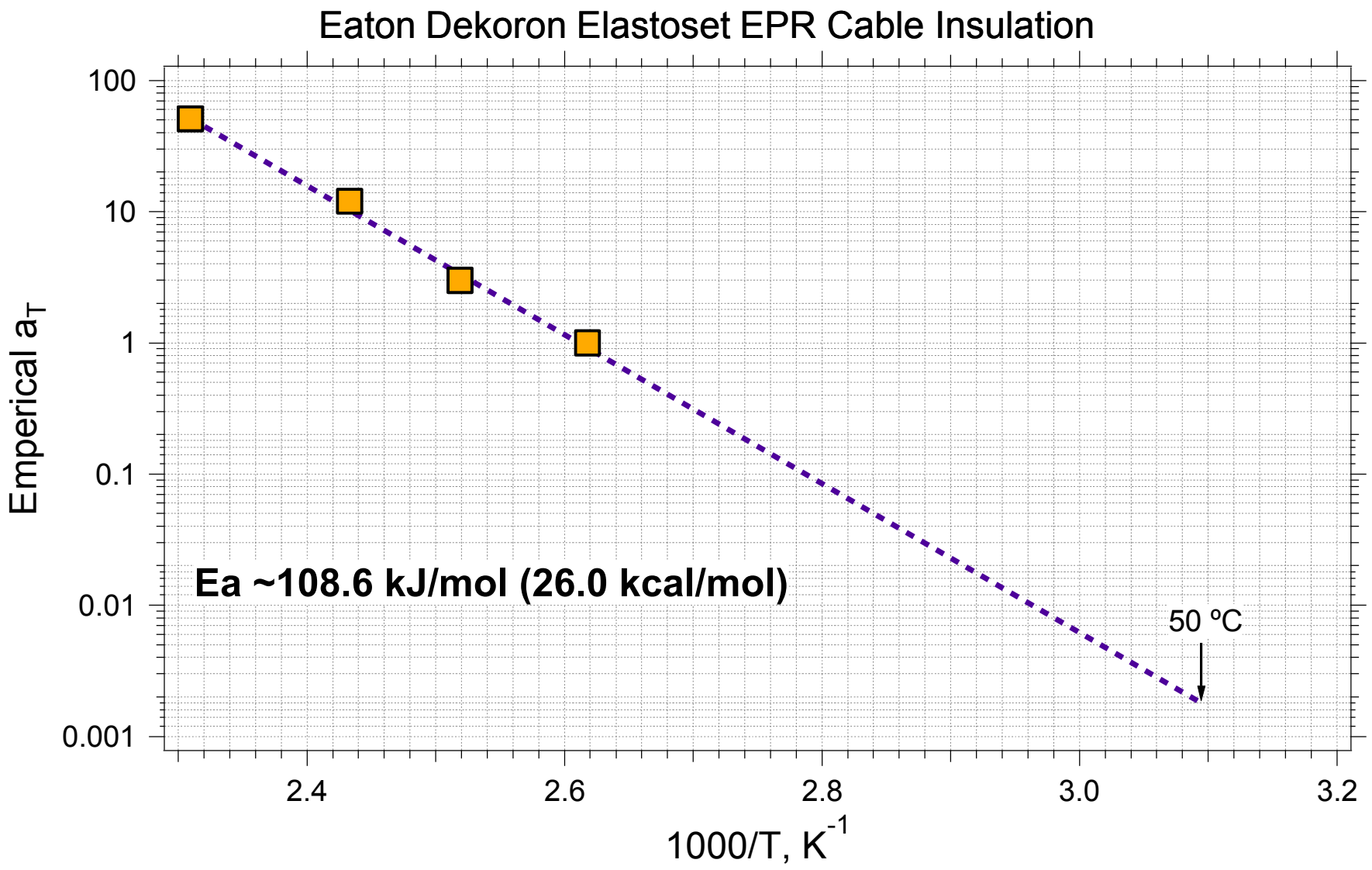
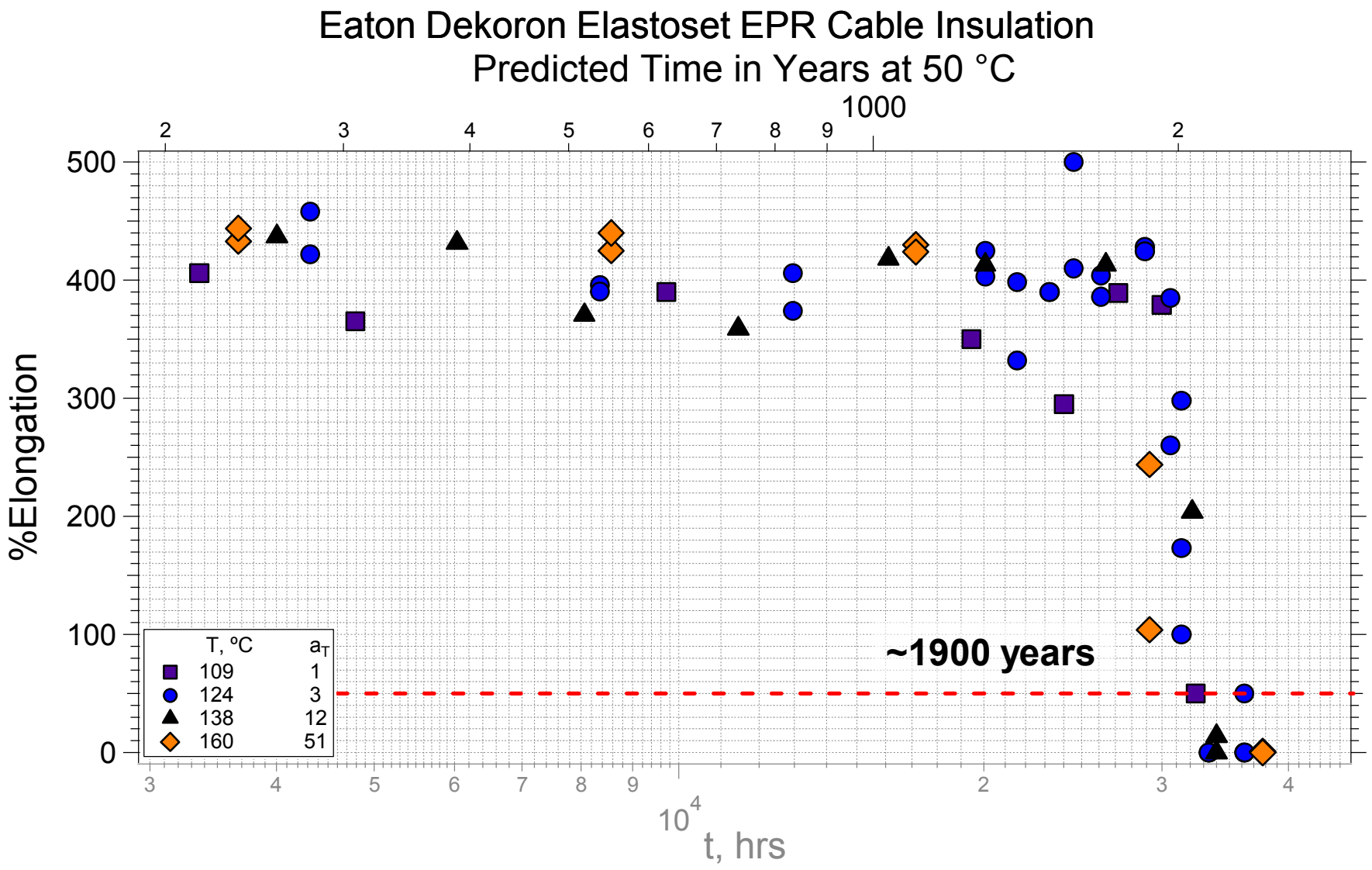


Thermal-Oxidative Prediction



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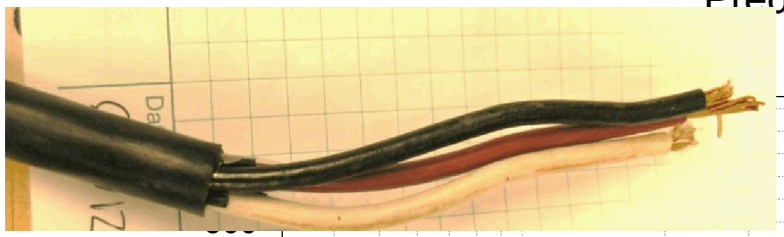
Field Returned Materials

MODEL VALIDATION

Wear Out Approach

Making Predictions is easy… Comparison of predictions with field returned data provides confidence in both the predictions and the methodologies employed in our aging programs.



Prediction employed E_A to be 101 kJ/mol

Ultimate tensile elongation data obtained from previous accelerated aging experiments on Anaconda *Durasheath* EPR cables. The data is plotted in predicted time at 27 C in years (shown in grey).

SAND2005-7331 K. T. Gillen, R. A. Assink, and R. Bernstein

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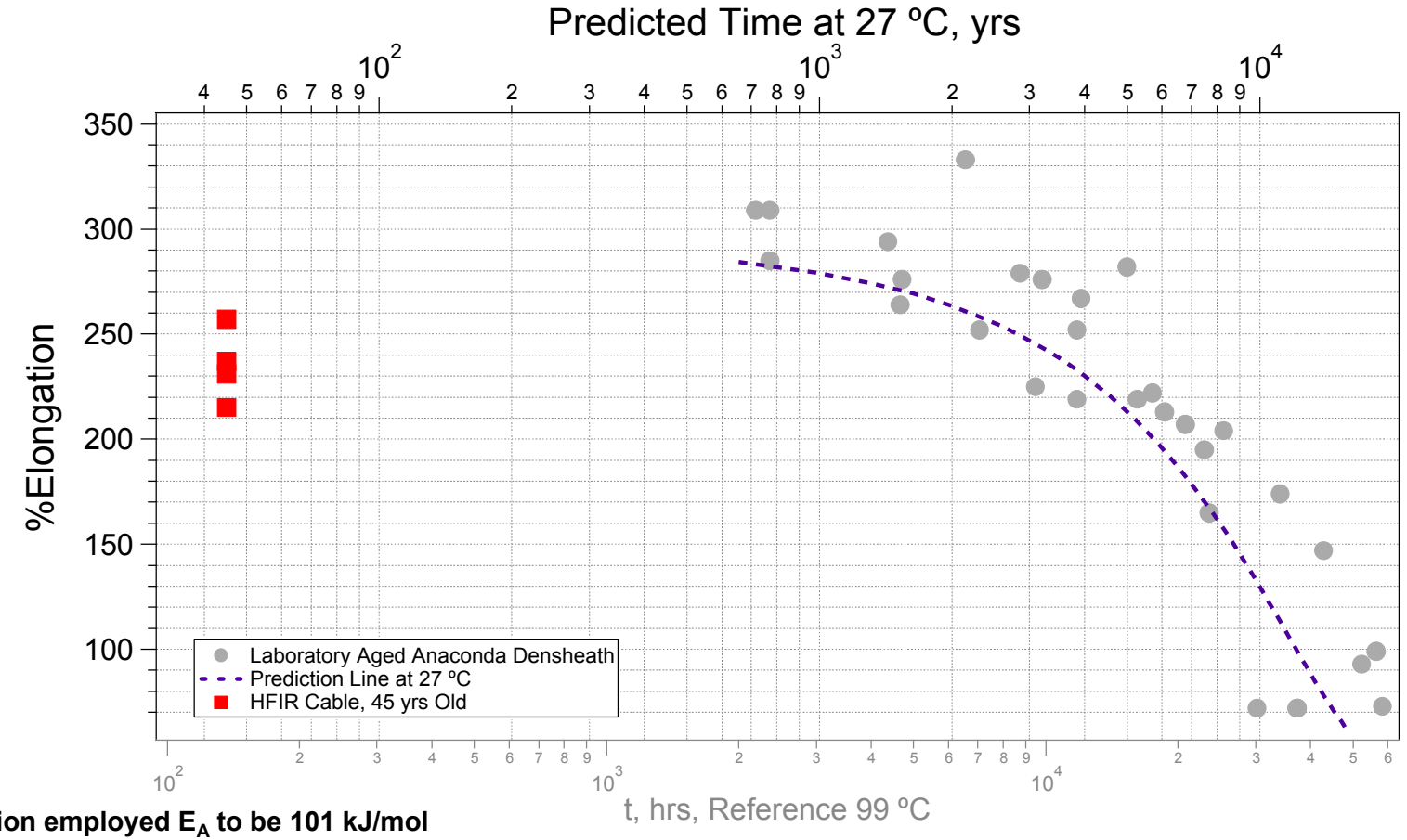

Prediction employed E_A to be 101 kJ/mol

Ultimate tensile elongation data obtained from previous accelerated aging experiments on Anaconda *Durasheath* EPR cables. The data is plotted in predicted time at 27 C in years (shown in grey). Ultimate tensile elongation data for Anaconda *Densheath* EPR cables returned from HFIR at ORNL (~45 yrs of age, T_{avg} ~ 27 °C, RH ~70%, shown in red).

Wear Out Approach

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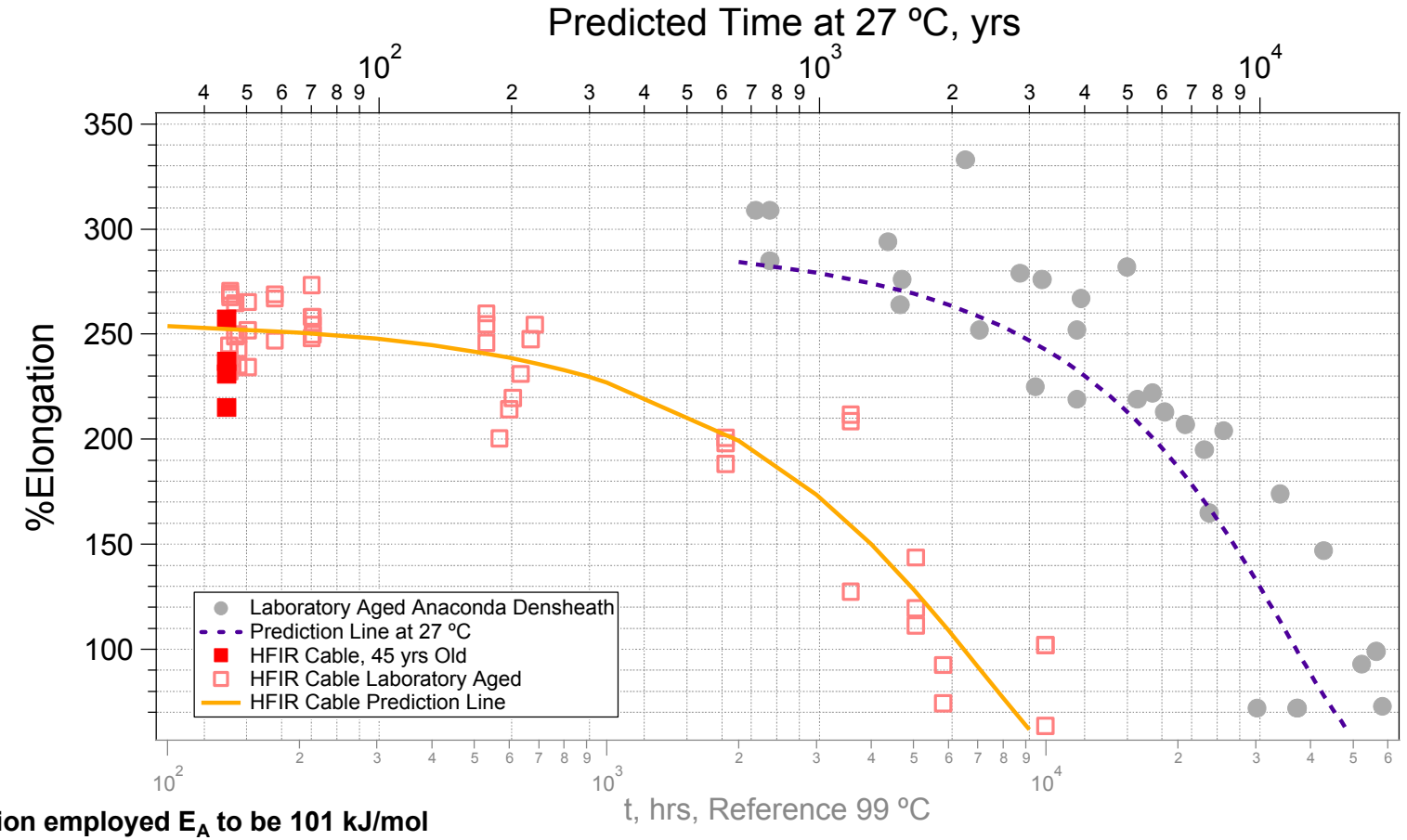
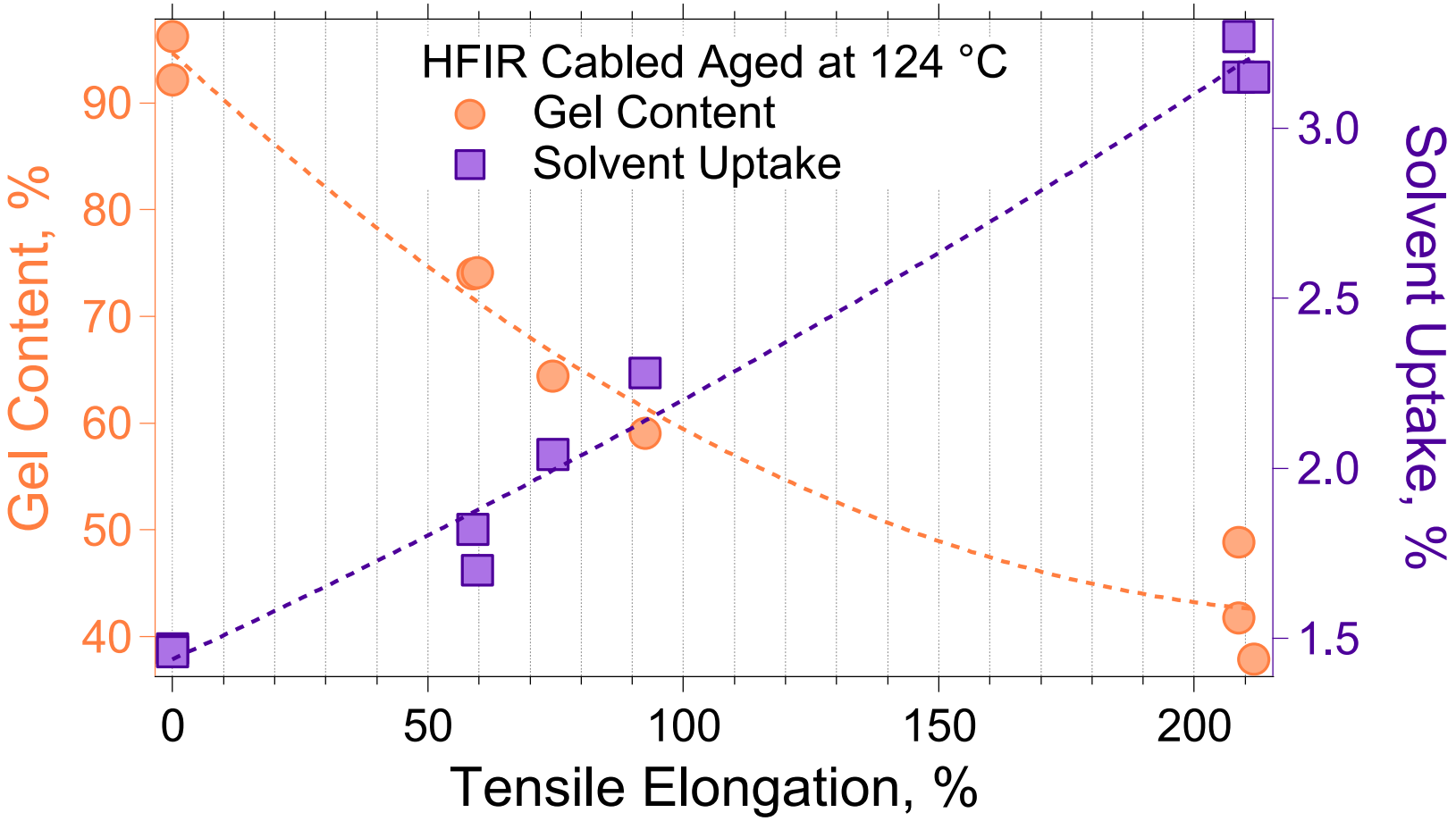


Prediction employed E_A to be 101 kJ/mol

Ultimate tensile elongation data obtained from previous accelerated aging experiments on Anaconda *Durasheath* EPR cables. The data is plotted in predicted time at 27 C in years (shown in grey). Ultimate tensile elongation data for Anaconda *Densheath* EPR cables returned from HFIR at ORNL (~45 yrs of age, T_{avg} ~ 27 °C, RH ~70%, shown in red) plotted with tensile data obtained from further aging of the HFIR cables.

Wear Out Approach

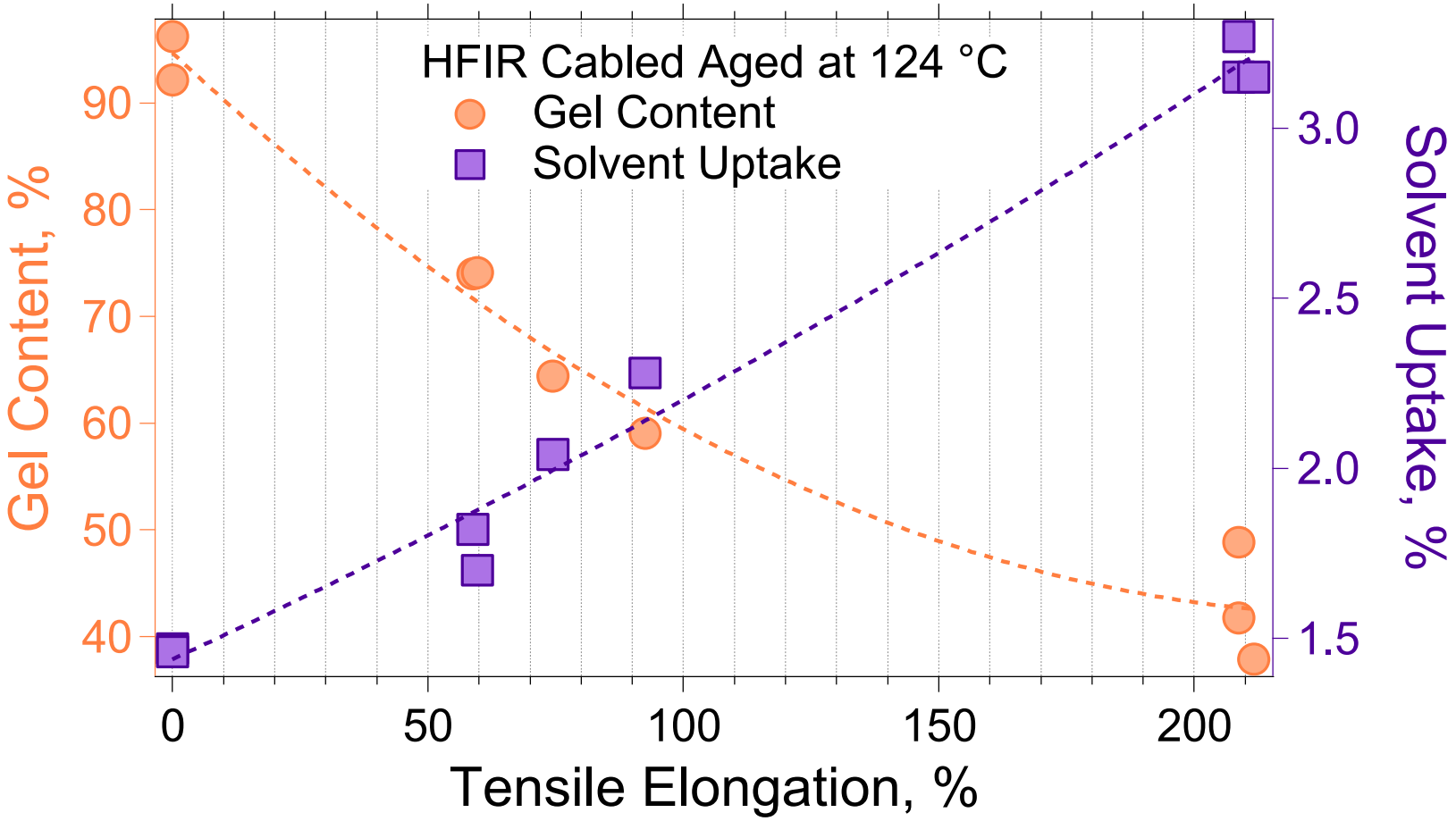
Making Predictions is easy… Comparison of predictions with field returned data provides confidence in both the predictions and the methodologies employed in our aging programs.



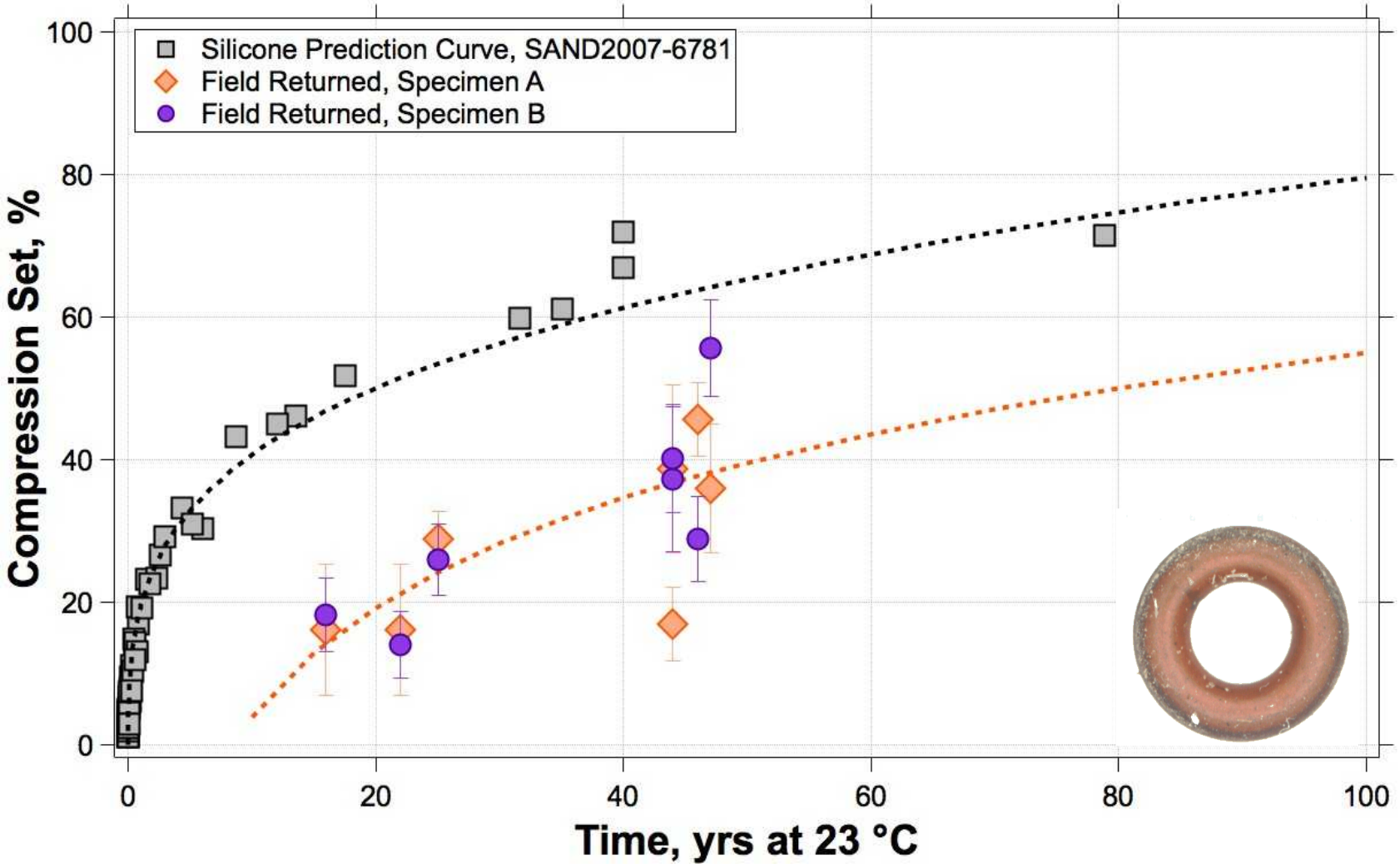
Wear Out Approach

Making Predictions is easy… Comparison of predictions with field returned data provides confidence in both the predictions and the methodologies employed in our aging programs.

<u>These results can be leveraged to develop condition monitoring techniques!</u>



Other Model Validation Examples



Other Model Validation Examples

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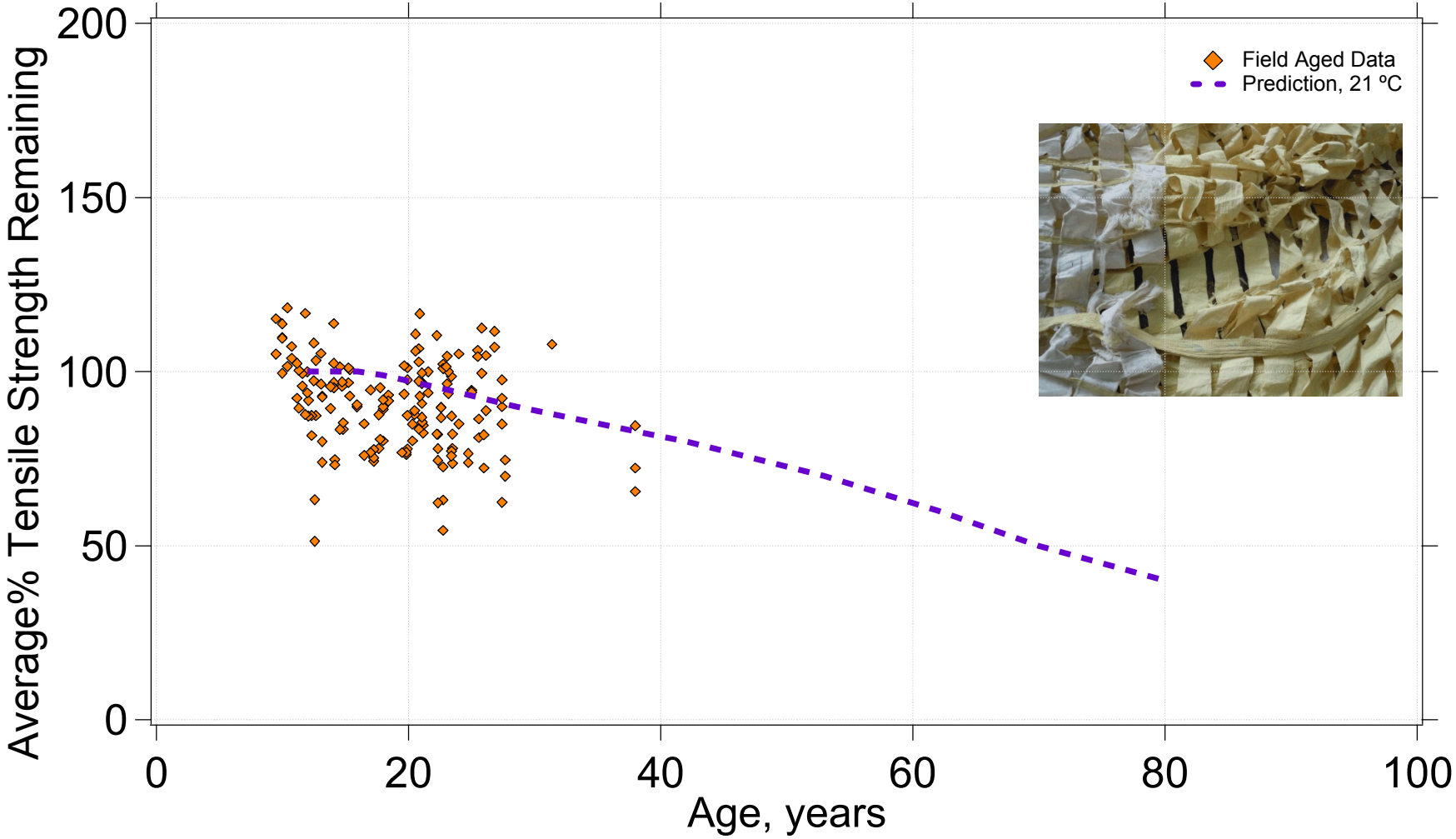
Textiles and Fibers!



White G. V., Bernstein, R.B., *"FY11 Materials Testing and Analysis"* Internal Memo, January 19, 2012

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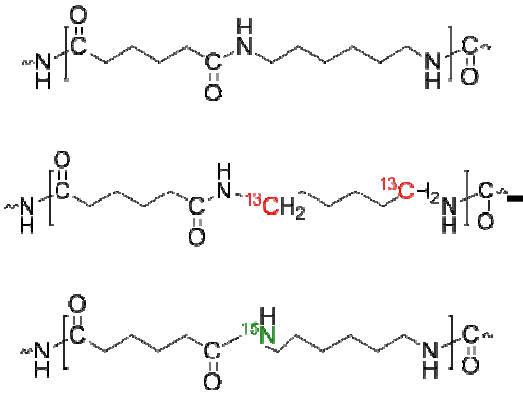
Isotopic Labeling

FUNDAMENTAL SCIENCE APPROACH

Outgassing Studies

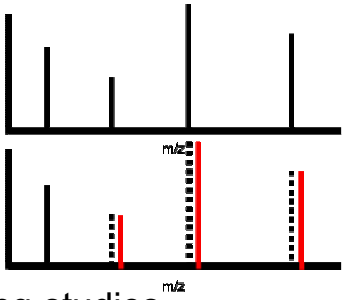


Isotopically labeled and unlabeled nylon 6.6 were aged in 5 cm^3 stainless steel vessels between 1 and ~450 days at RT and 138 °C

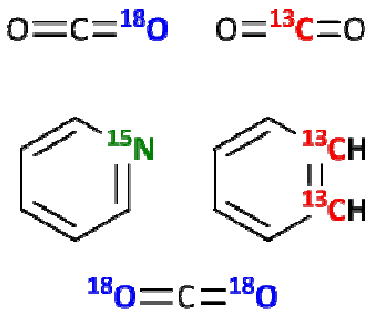
Cryo-GC/MS

Identify degradation products

Monitor mass spectra for shifts



Use mass shifts to determine degradation



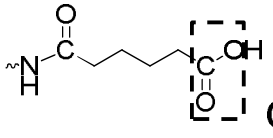
Caveat: It is critical to employ ***well characterized*** polymers in your aging studies

White et al. *Poly. Deg. Stab.* 97, 1396, *2012*
Smith et al. *J. Am. Soc. Spectr.* 23, 1579, 2012

Quantitative Analysis of CO_2 Formation

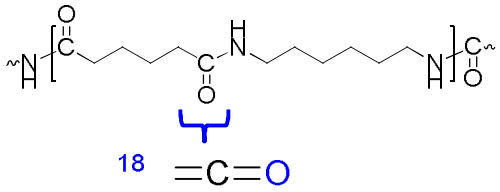
m/z	Assignment	Relative MS Intensity (%)	Functional Group
44	$CO_2^{+\bullet}$	17.6 ± 0.5	Chain End
46	$CO^{18}O^{+\bullet}$	42.3 ± 2.7	Amide Carbonyl
48	$C^{18}O^{18}O^{+\bullet}$	40.1 ± 3.3	Methylene

CO_2 Products formed when aged in $^{18}O_2$



Chain End → Unlabeled CO_2

O=C=O



Amide Carbonyl → mono-labeled CO_2

White et al. *Poly. Deg. Stab. 97*, 1396, *2012*

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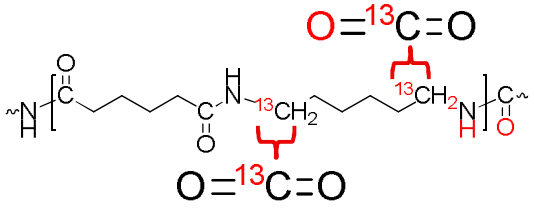
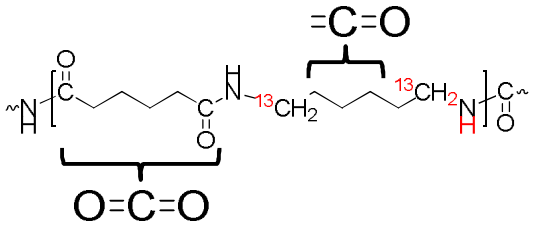
m/z	Assignment	Relative MS Intensity (%)	Functional Group
44	$CO_2^{+\bullet}$	85.4 ± 0.2	Methylene
45	$^{13}CO_2^{+\bullet}$	14.6 ± 0.2	*N*-Vicinal Methylene

CO_2 Products formed when aged in air



N-Vicinal Methylene → ^{13}C labeled CO_2



Methylene → Unlabeled CO_2

White et al. *Poly. Deg. Stab. 97*, 1396, *2012*

Quantitative Analysis of CO_2 Formation

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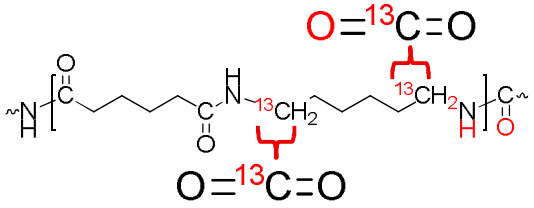
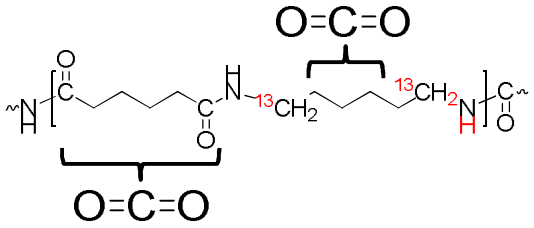
<u>CO_2 Products formed when aged in air</u>



N-Vicinal Methylene → ^{13}C labeled CO_2



Methylene → Unlabeled CO_2

40% of CO_2 comes from the methylene groups
15% of all CO_2 comes from the *N*-Vicinal methylene groups
25% of all CO_2 comes from all other methylene groups

White et al. *Poly. Deg. Stab. 97*, 1396, *2012*

Quantitative Analysis of CO_2 Formation

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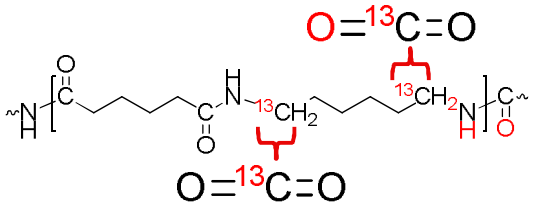
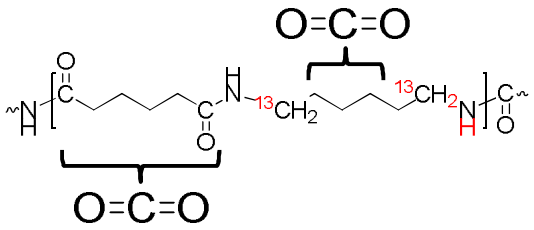
45	$^{13}CO_2^{+\bullet}$	14.6 ± 0.2	*N*-Vicinal Methylene

CO_2 Products formed when aged in air



N-Vicinal Methylene → ^{13}C labeled CO_2



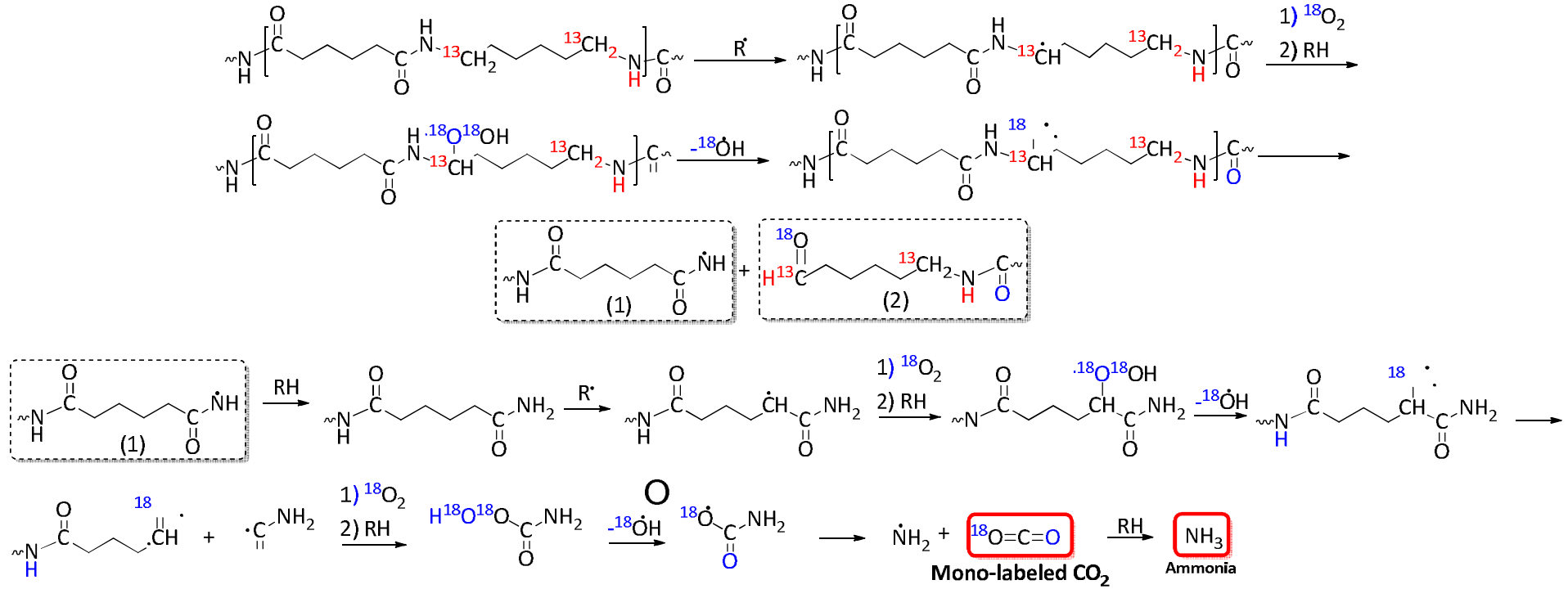
Methylene → Unlabeled CO_2

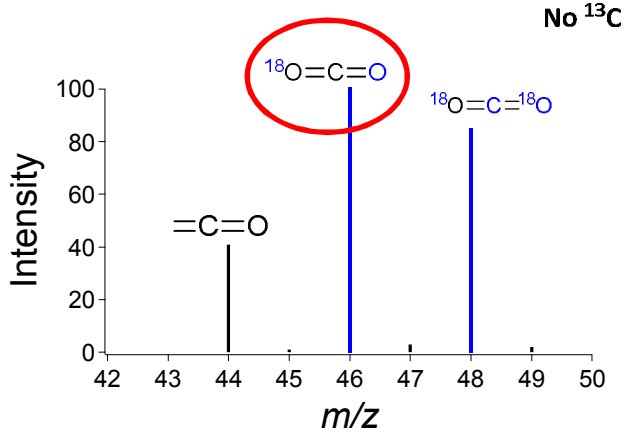
40% of CO_2 comes from the methylene groups
15% of all CO_2 comes from the *N*-Vicinal methylene groups
25% of all CO_2 comes from all other methylene groups

N-Vicinal methylene groups contribute 38% of CO_2 formed from the methylene groups
The other four types of methylene groups contribute 16% each to the CO_2 formed from the methylene groups.
The most labile hydrogen in the nylon backbone is therefore in the *N*-Vicinal methylene group.

White et al. *Poly. Deg. Stab. 97*, 1396, *2012*

Initiation at the N-Vicinal Methylene Group





Note that the ^{13}C and ^{18}O experiments were run <u>separately</u>. Outcomes are shown together in this presentation in order to save space.

White et al. *Poly. Deg. Stab. 97*, 1396, *2012*

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Thank you for your attention!

QUESTIONS?