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Degradation studies of Nylon and Kevlar

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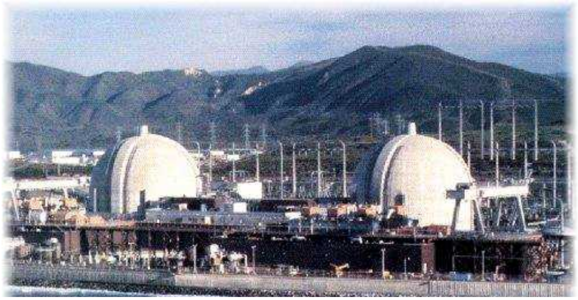
National Nuclear Security Administration

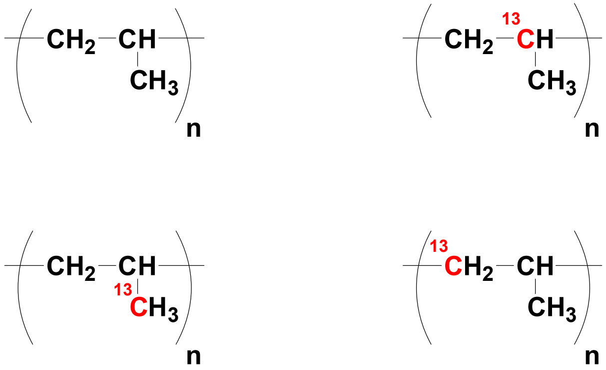
Organic Materials Aging and Degradation

O-rings

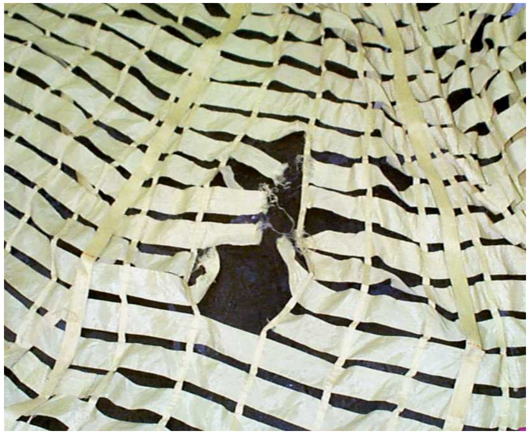


Nuclear Power Plant Cable Insulation

Aircraft Wire Insulation



Labeled Polypropylene



Textiles

Deception!

Results from initial high temperature, short times (even out to 1 year) accelerated aging can be misleading.

Chemistry / mechanisms must be understood.

Approach/Goals

Macroscopic level

Physical property

Tensile Property

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

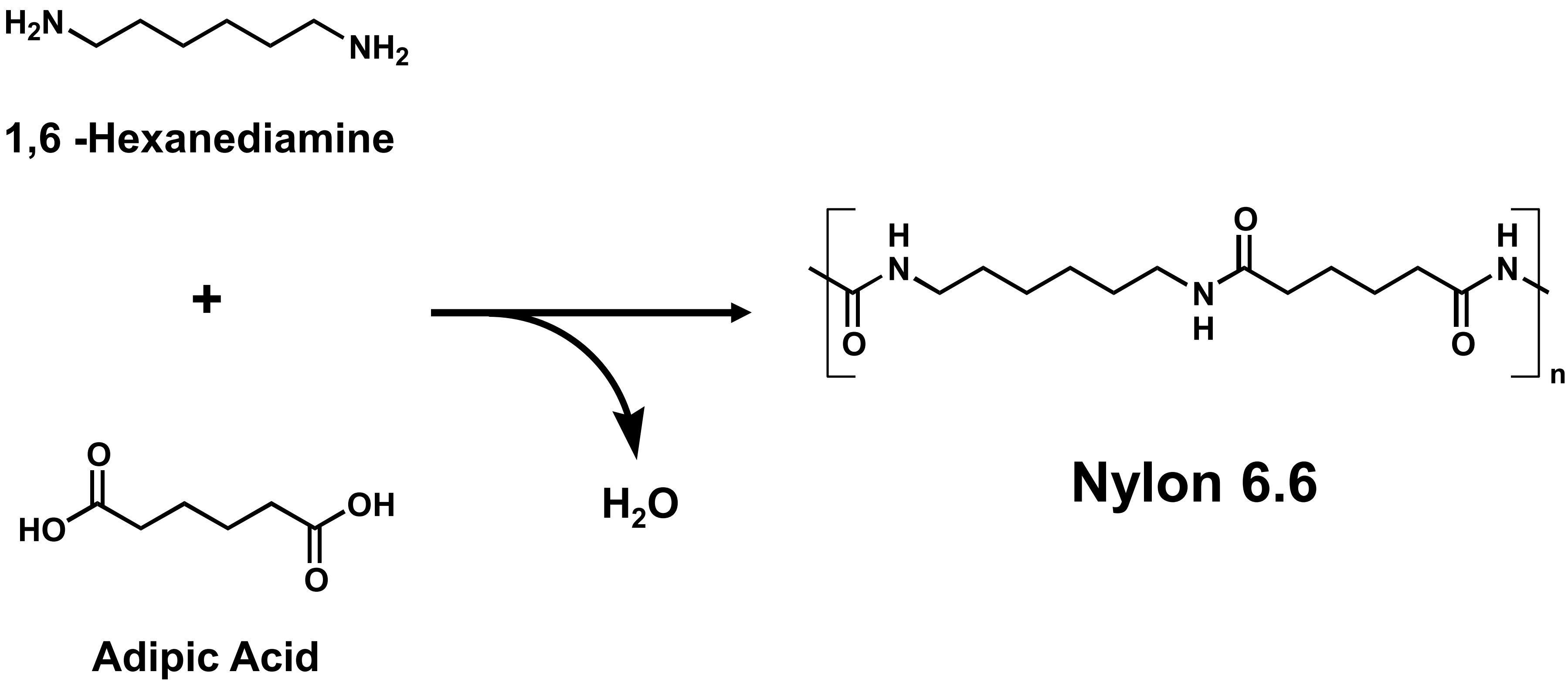
GPC

Goals

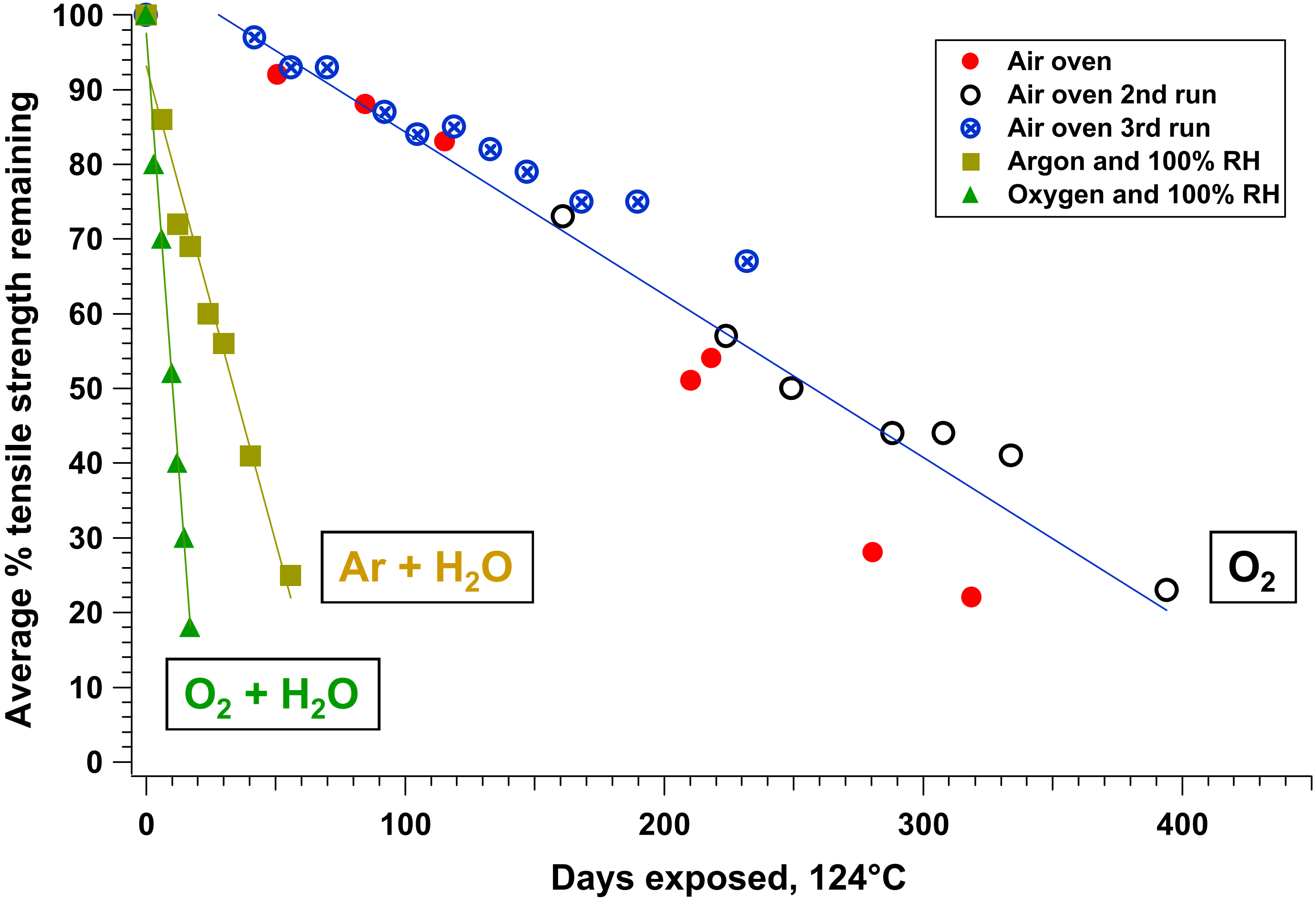
- Prediction of physical properties vs. time
    - Predict remaining lifetime of field materials
- Develop condition monitoring method

Nylon Structure

Vulnerable to degradation via oxygen and water



Nylon Tensile Comparison



(1) Bernstein, R.; Derzon, D. K.; Gillen, K. T. Polymer Degradation and Stability, Nylon 6.6 accelerated aging studies: thermal-oxidative degradation and its interaction with hydrolysis 2005, 88, 480-488.
(2) Bernstein, R.; Derzon, D. K.; Gillen, K. T. Polymer Preprints (American Chemical Society, Division of Polymer Chemistry), Nylon degradation studies: Humidity and aging 2002, 43, 1349.

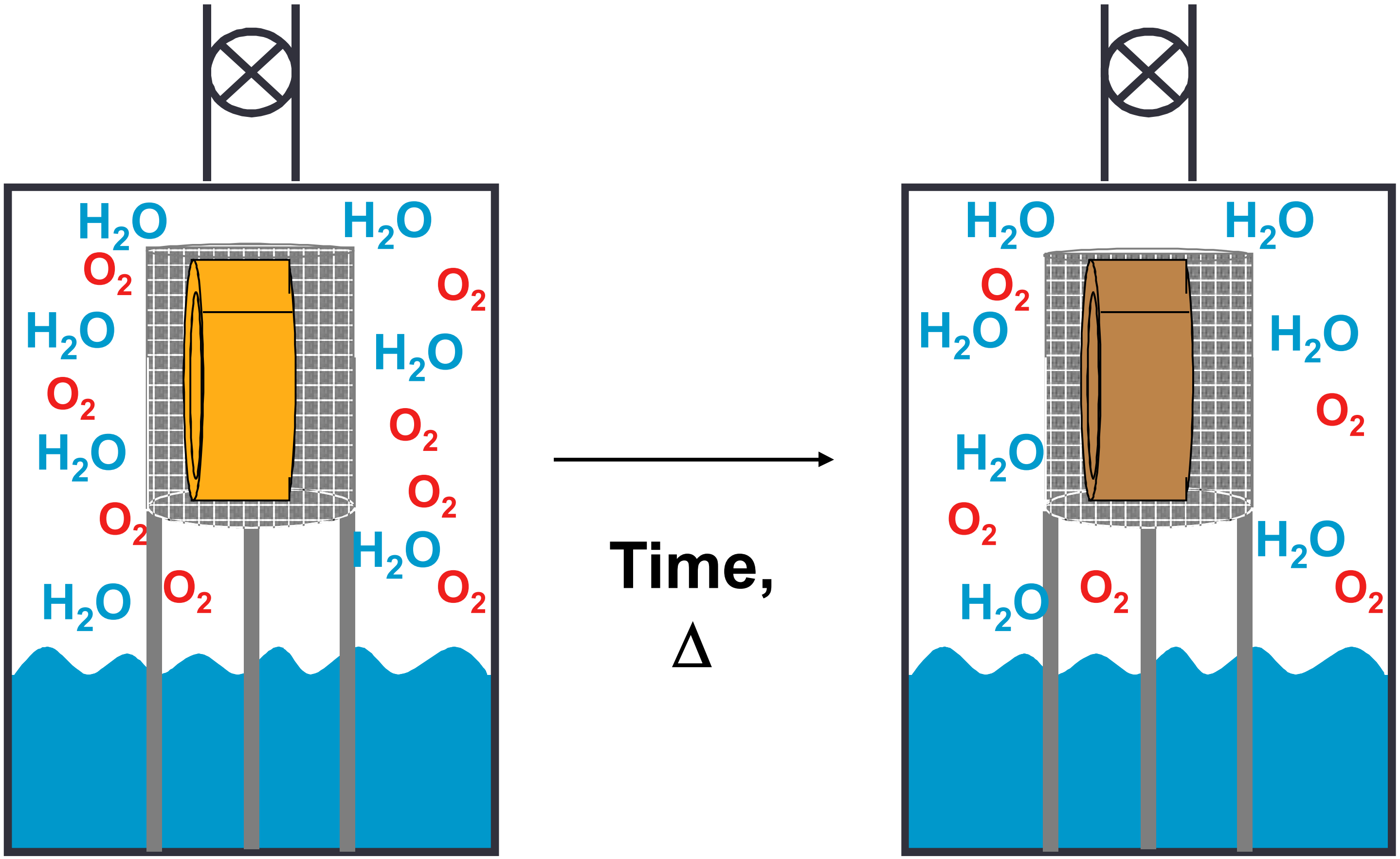
Nylon Tensile Comparison

Conditions	Normalized Rate (Slope) 124 ºC
Rate for Thermal and Oxygen	1.0
Rate for Thermal, Argon, and 100% R_H	7.4
Rate for Thermal, Oxygen, and 100% R_H	22.9

8.4

Combined rate ca. 3 times sum of individual rates

Humidity Aging Schematic



Humidity Aging Hardware

Time-Temperature Superposition

Does mechanism change as a function of temperature?

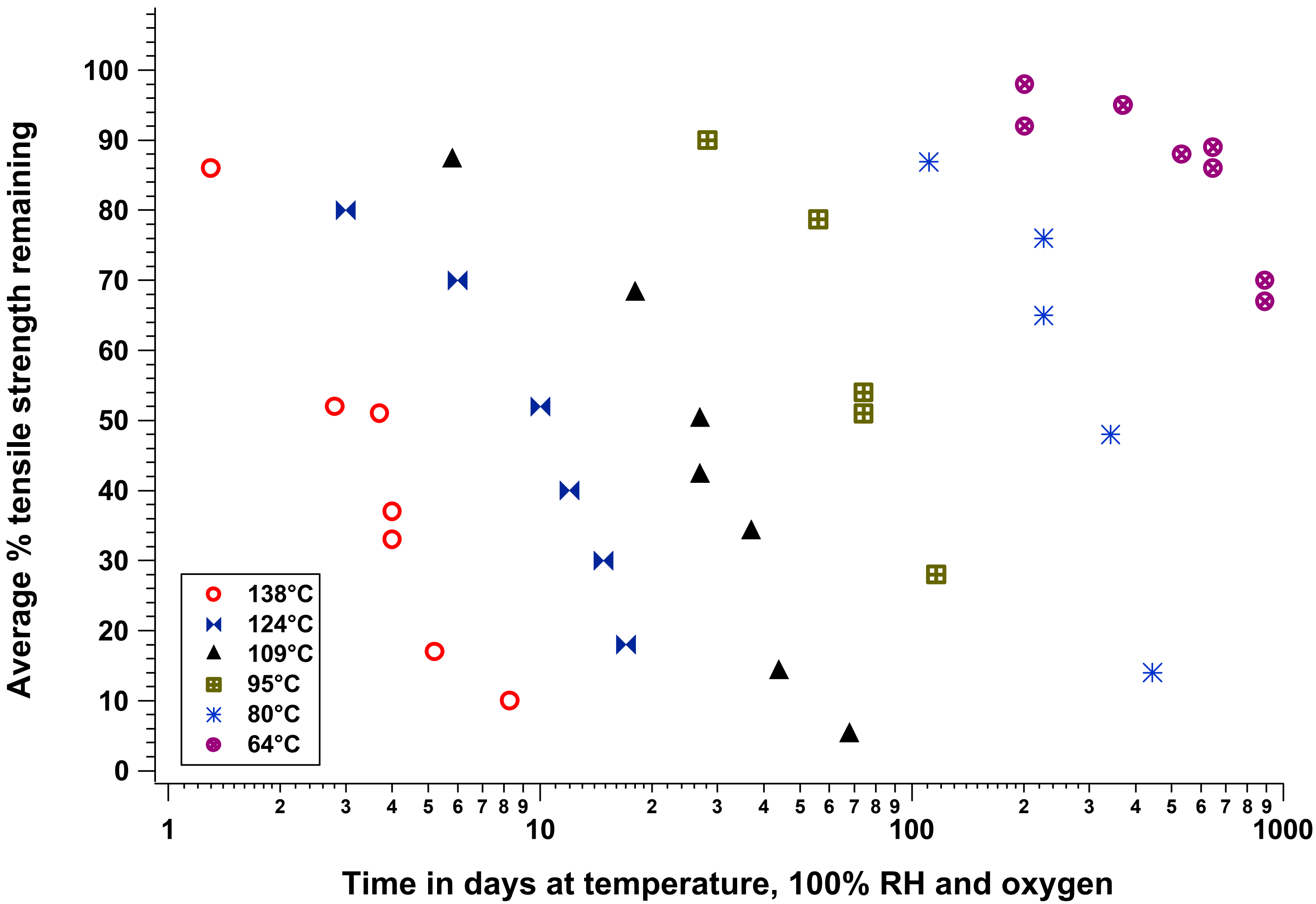
If same mechanism:

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

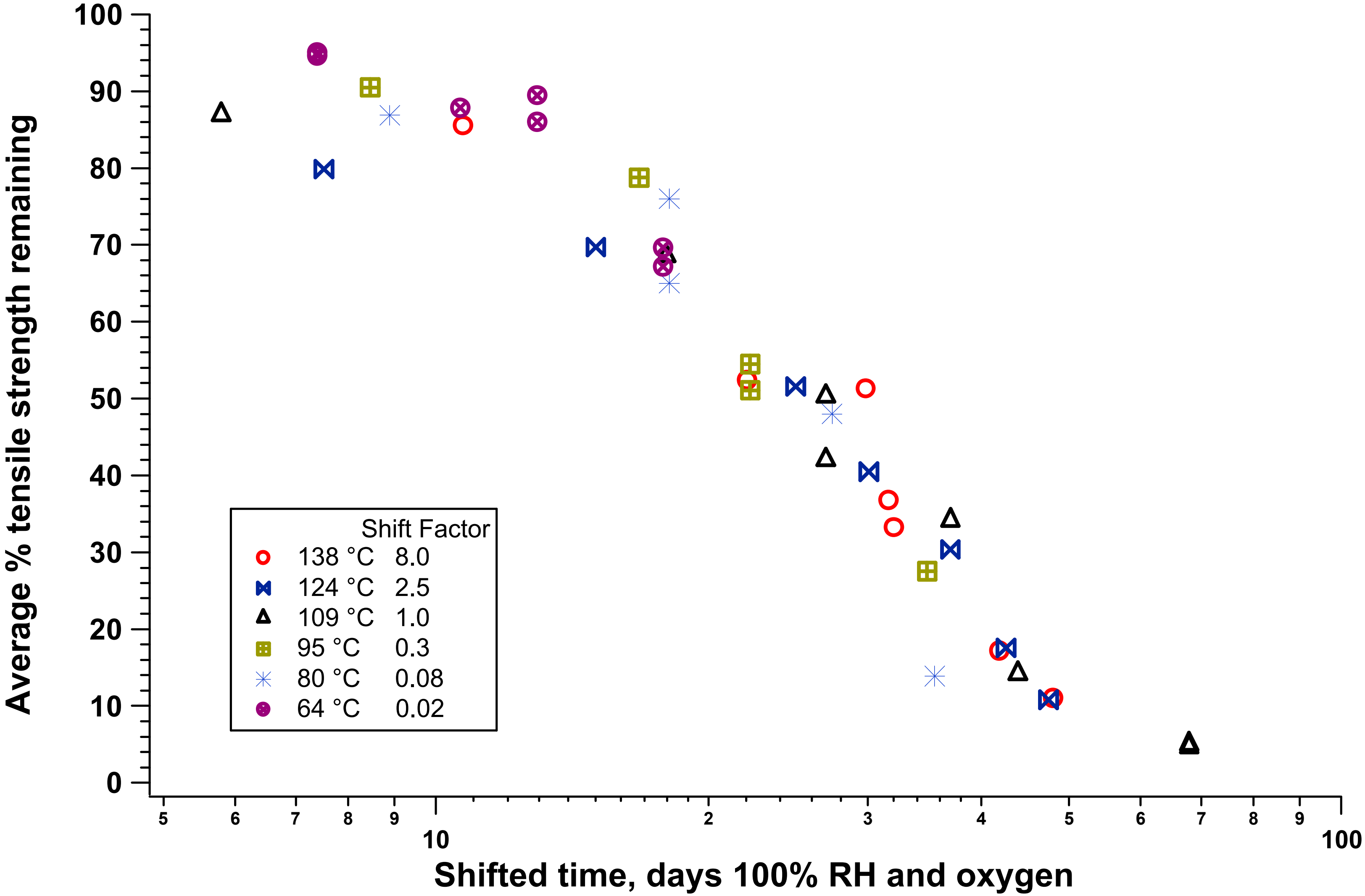
1. Pick a reference temperature
2. Multiply the time at each temperature by the constant that gives the best overlap with the reference temperature data
3. Define that multiple as 'a_T' ($a_T = 1$ for ref. temp.)
4. Find a_T for each temperature

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

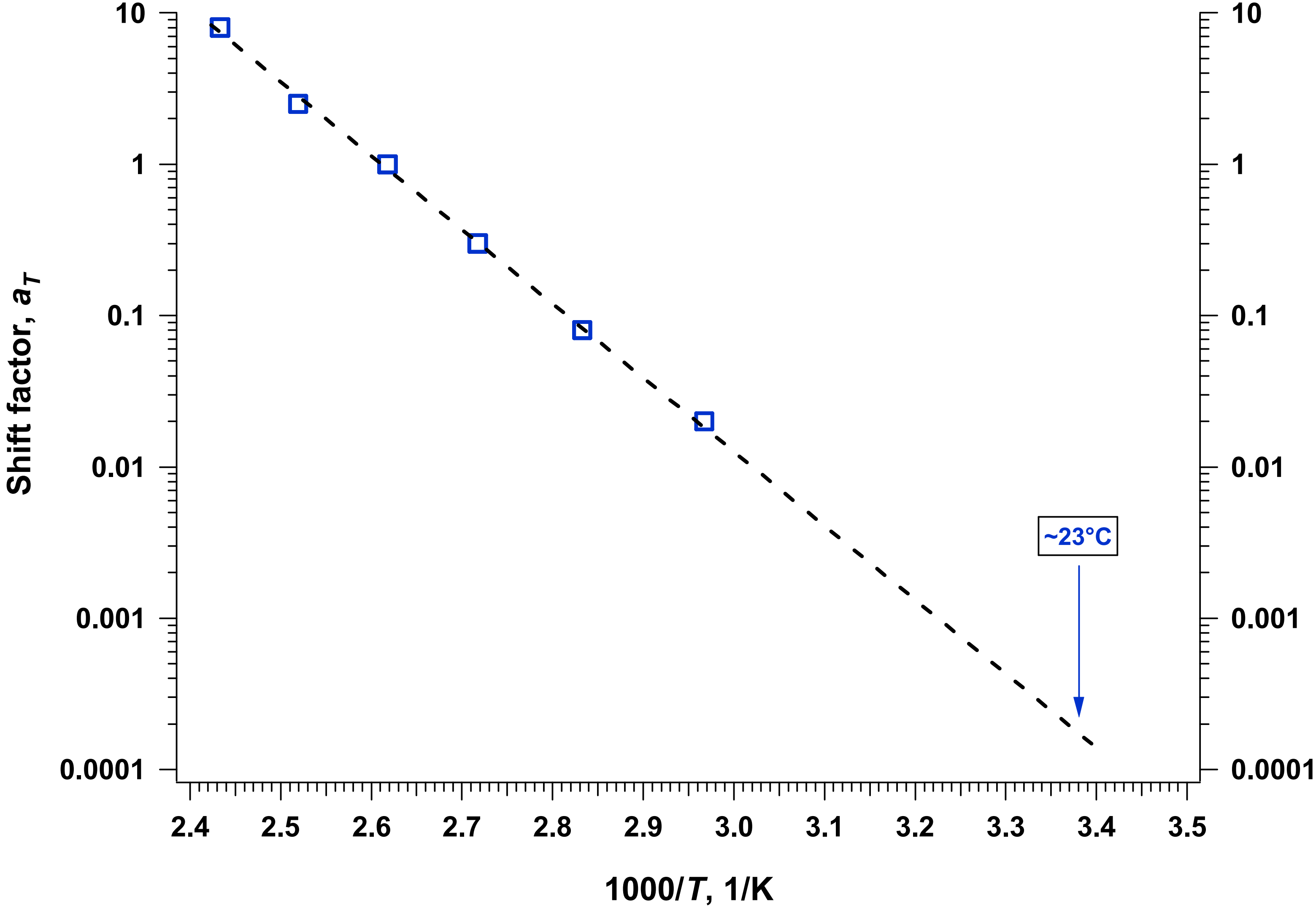
Nylon 100% RH O_2



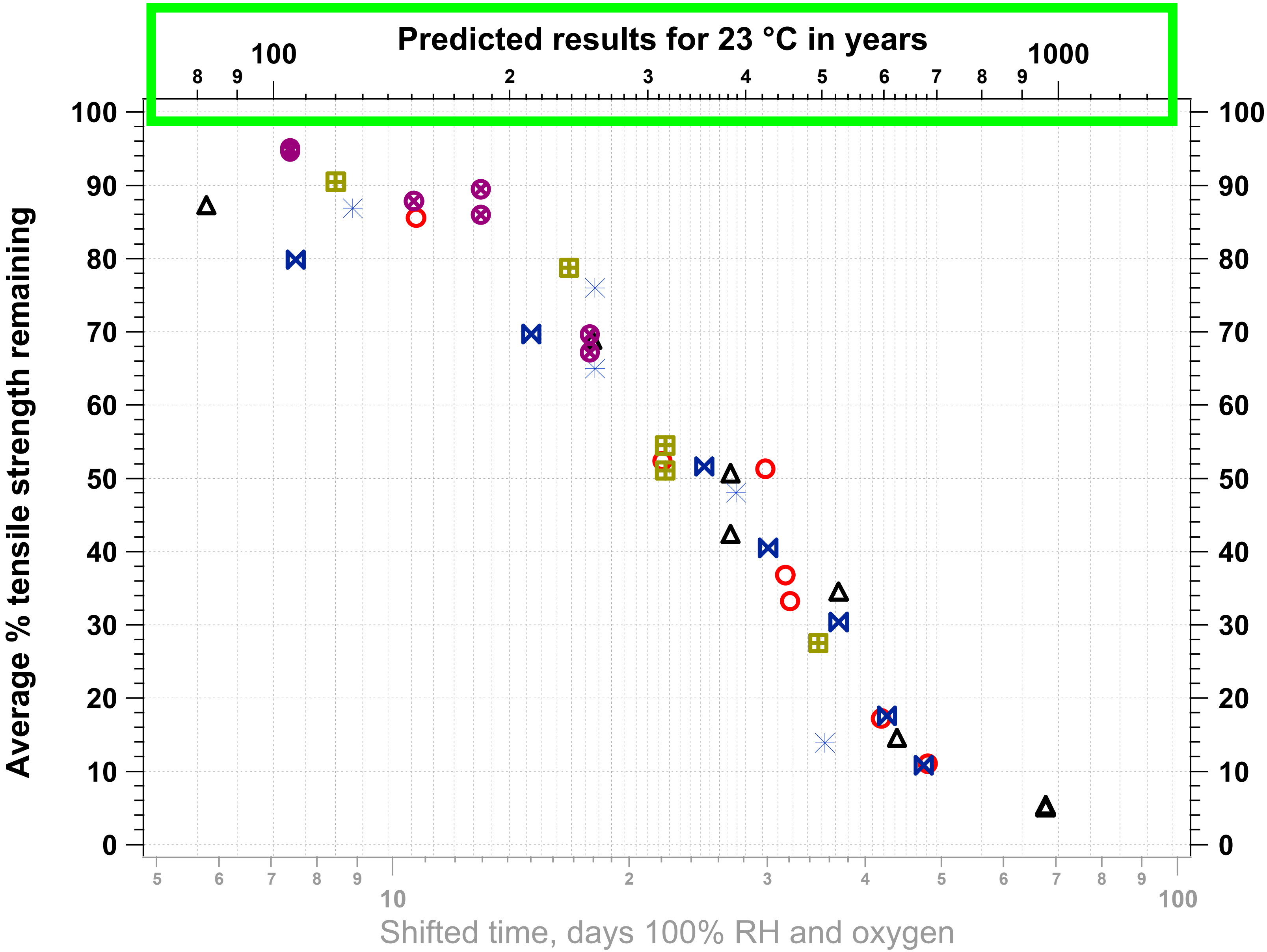
Shifted Nylon 100% RH O_2



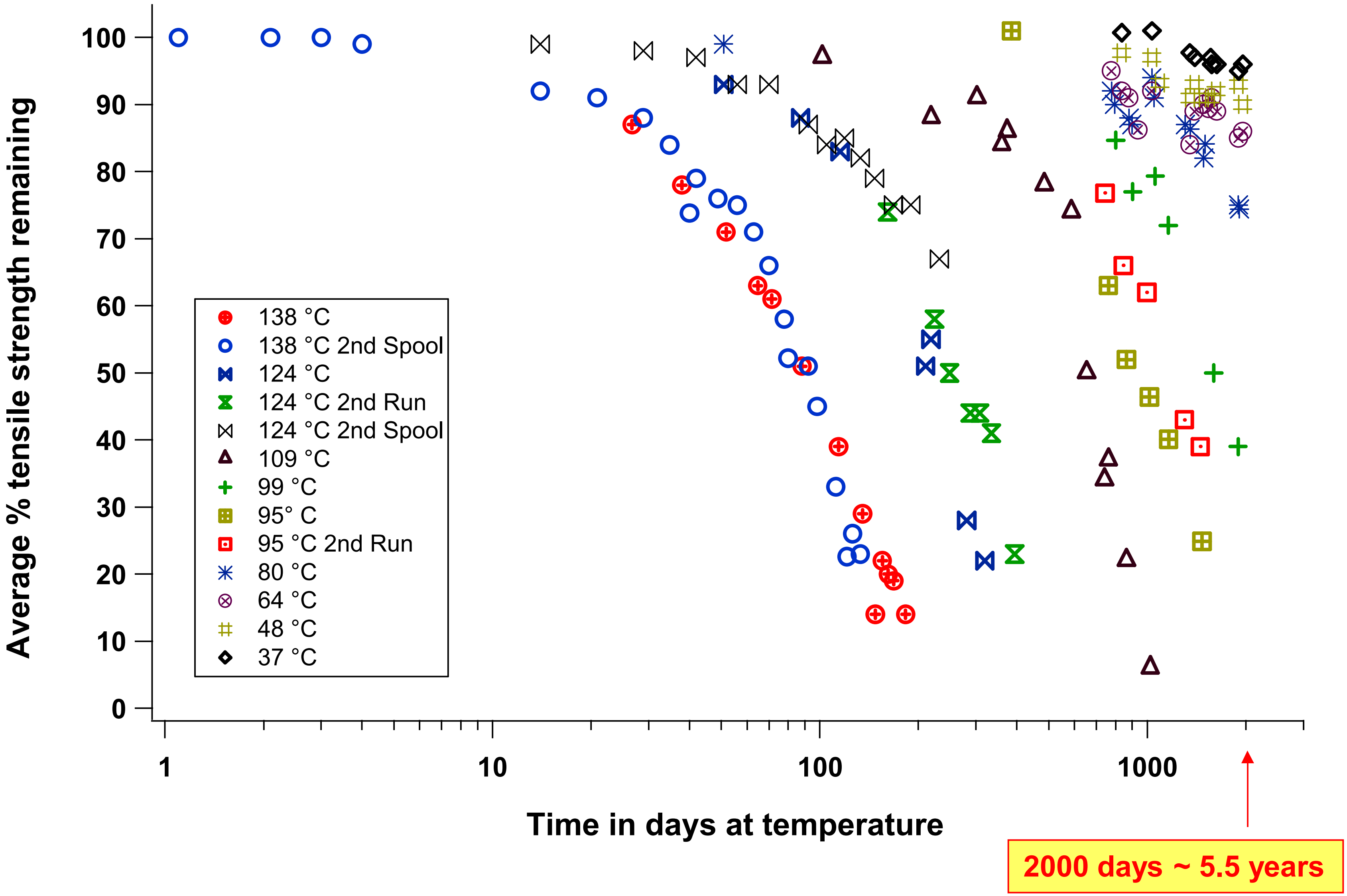
Shift Factors Nylon 100% RH O_2



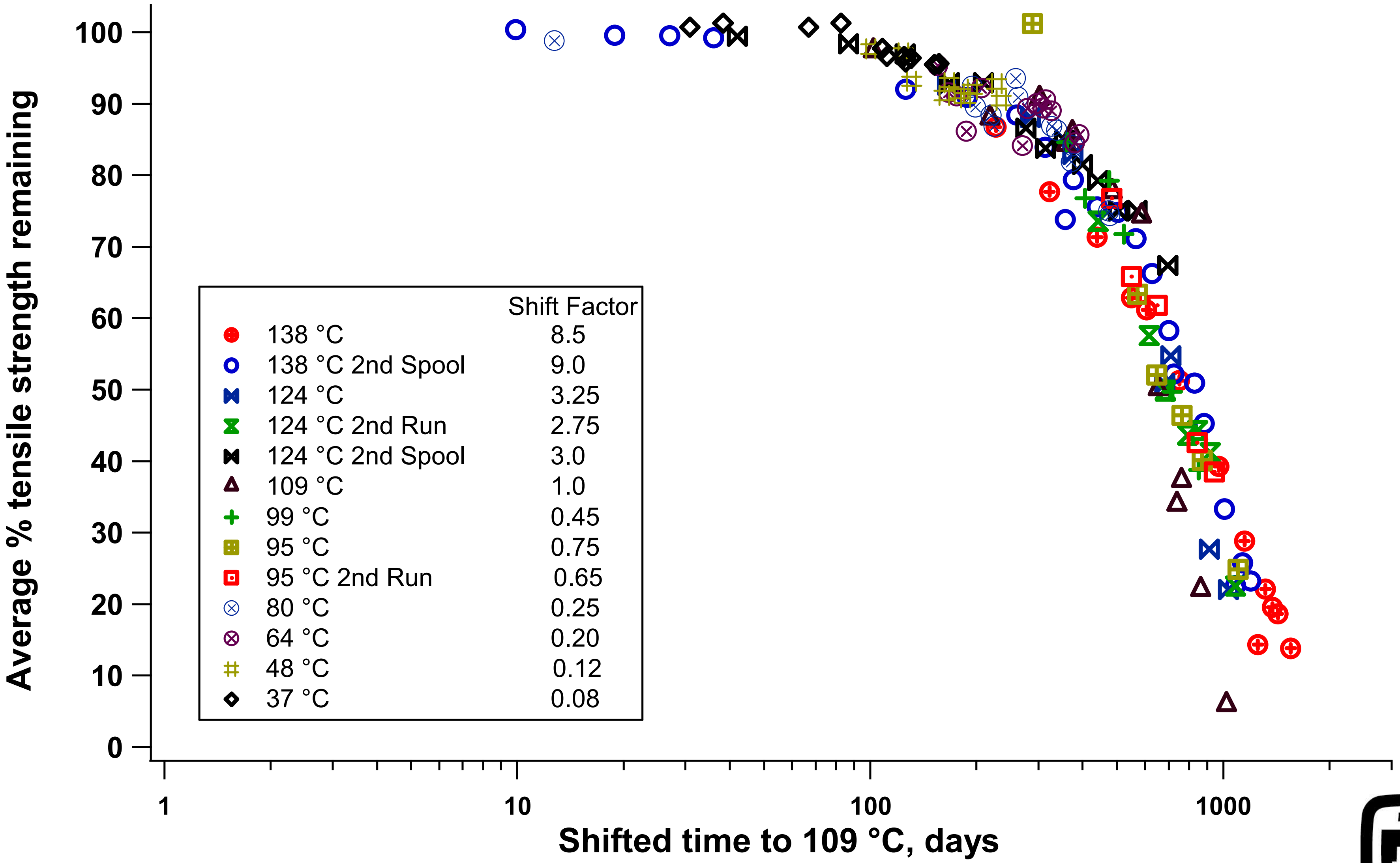
Predicted Tensile Strength; Nylon 100% RH O_2 at 23 °C



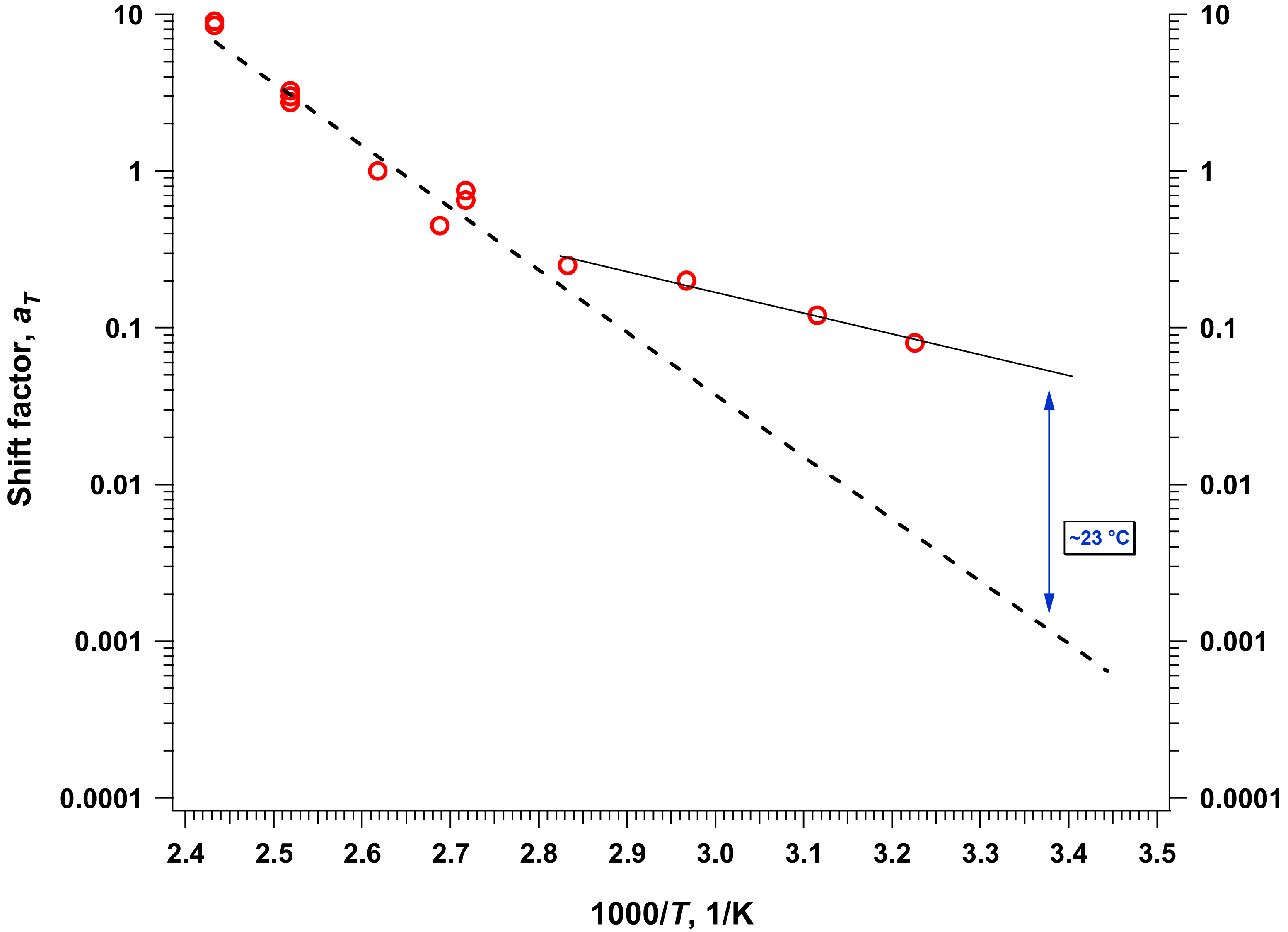
Thermal-oxidative Aging: Nylon



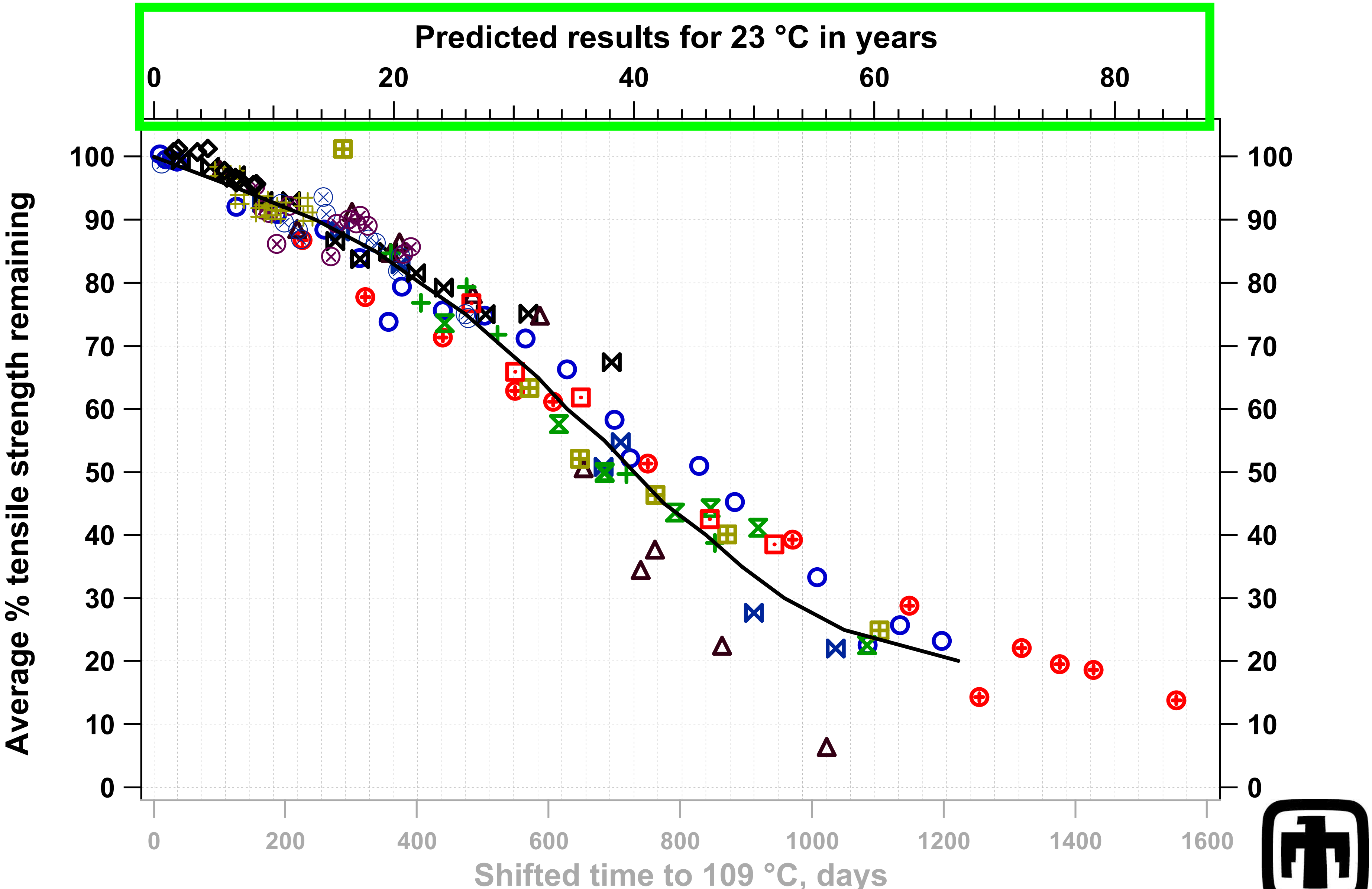
Thermal-oxidative Aging: Nylon Shifted Data



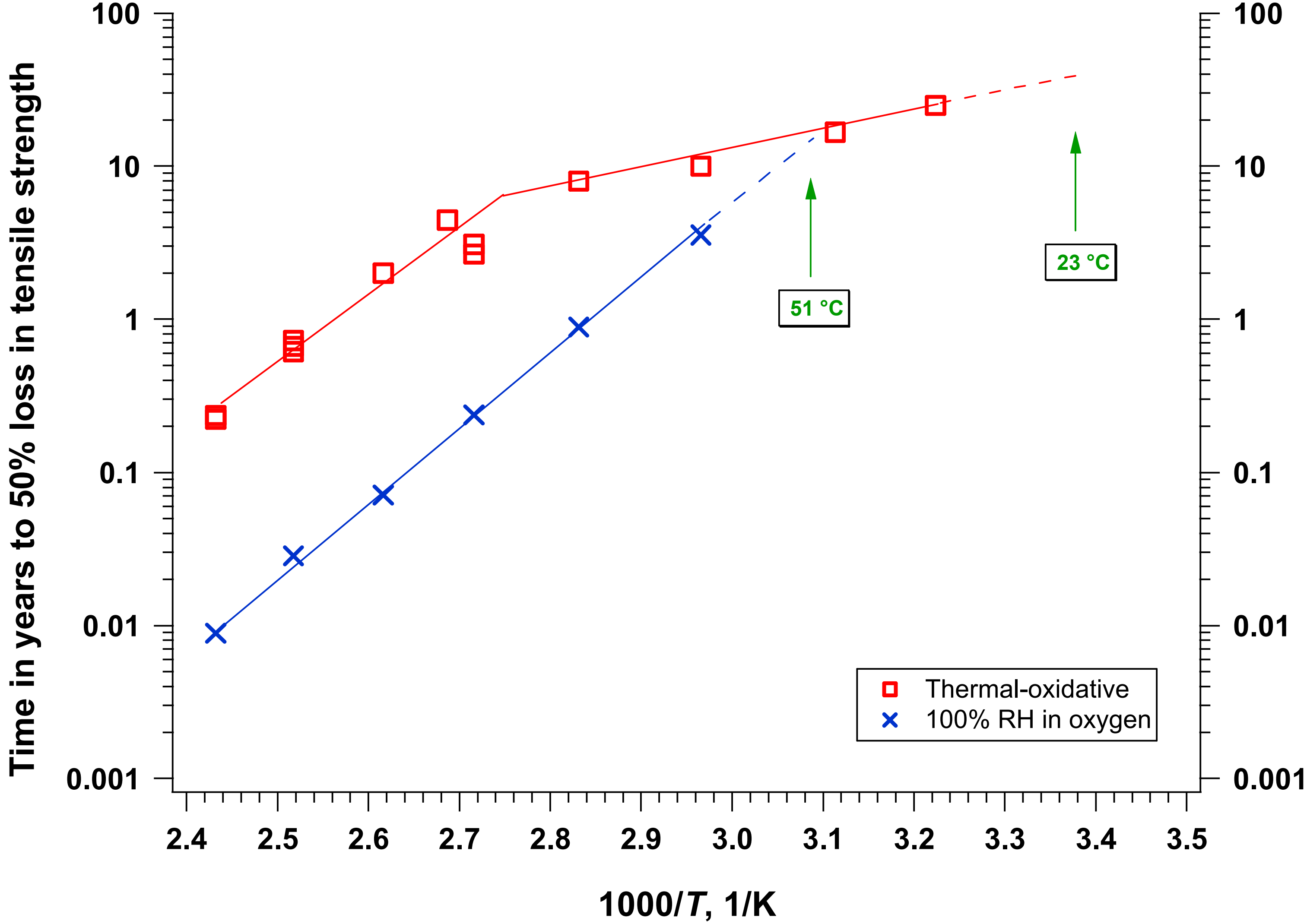
Thermal-oxidative Aging: Nylon Shift Factor Graph



Thermal-oxidative Aging: Nylon Shifted Data



Thermal-oxidative and Humidity Comparison



Thermal Exposure

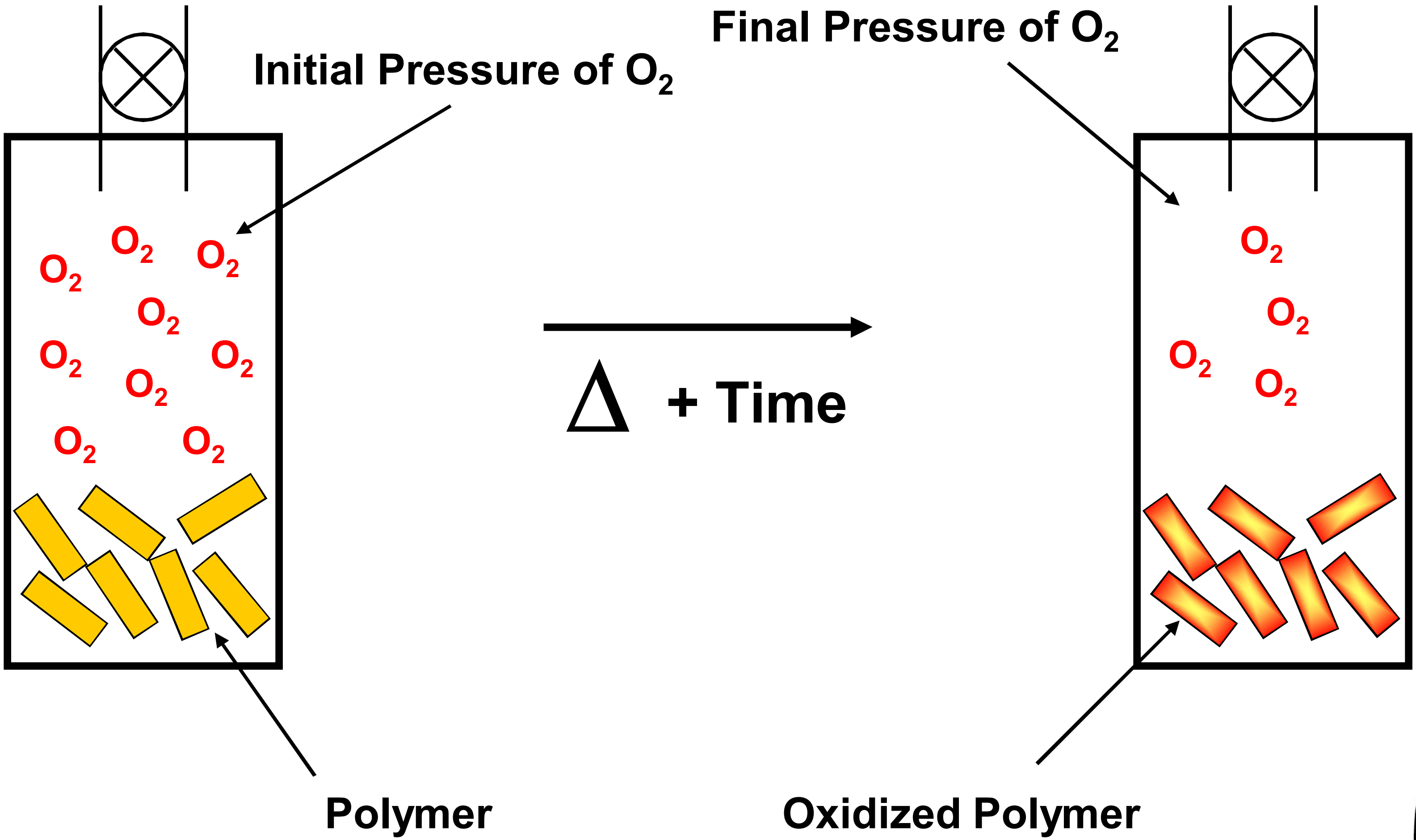
Thermal-Oxidation

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

Quantify amount of oxygen consumed

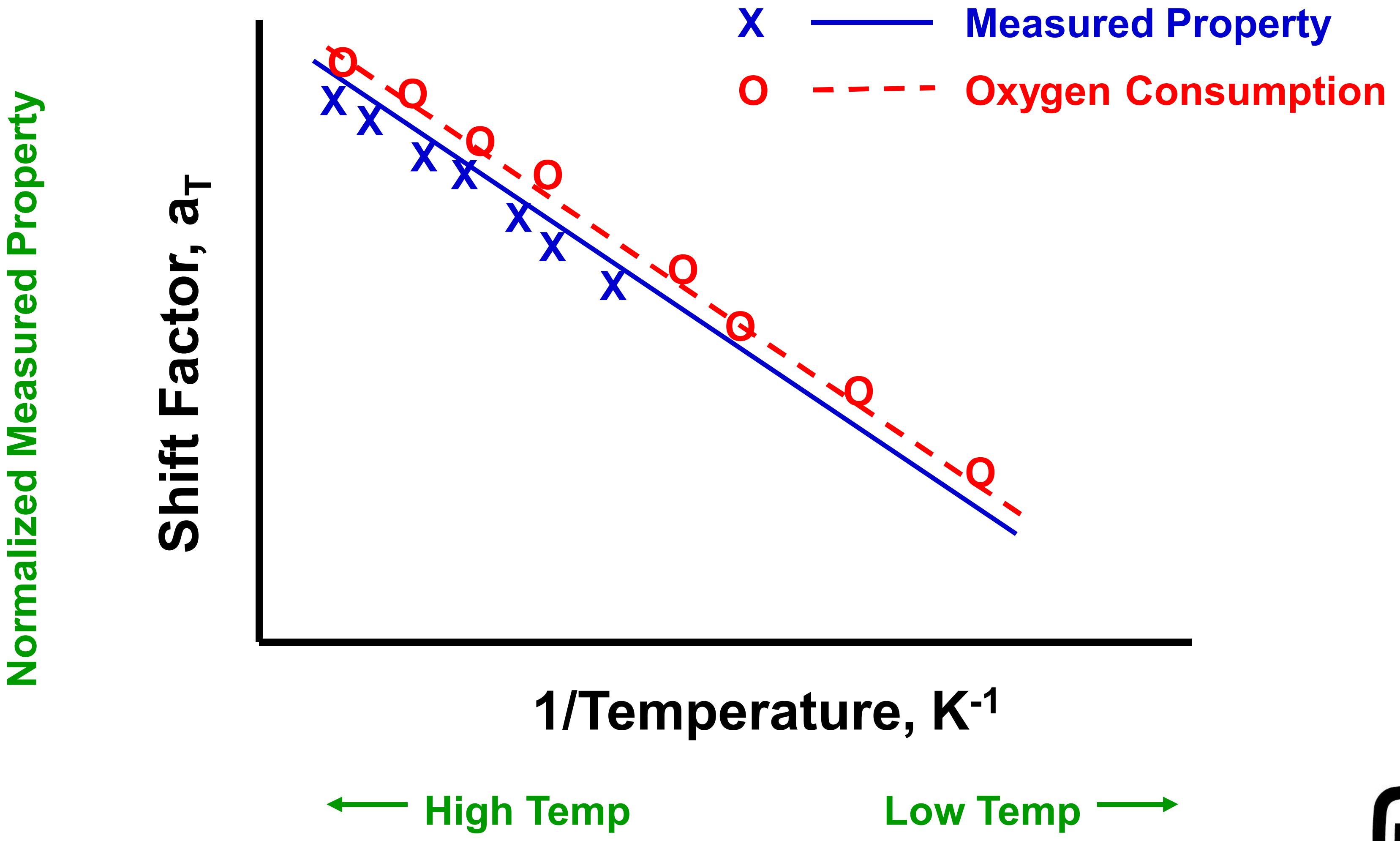
- Simple in theory
- Difficult in practice
- Amazingly sensitive

Schematic of Oxuptake

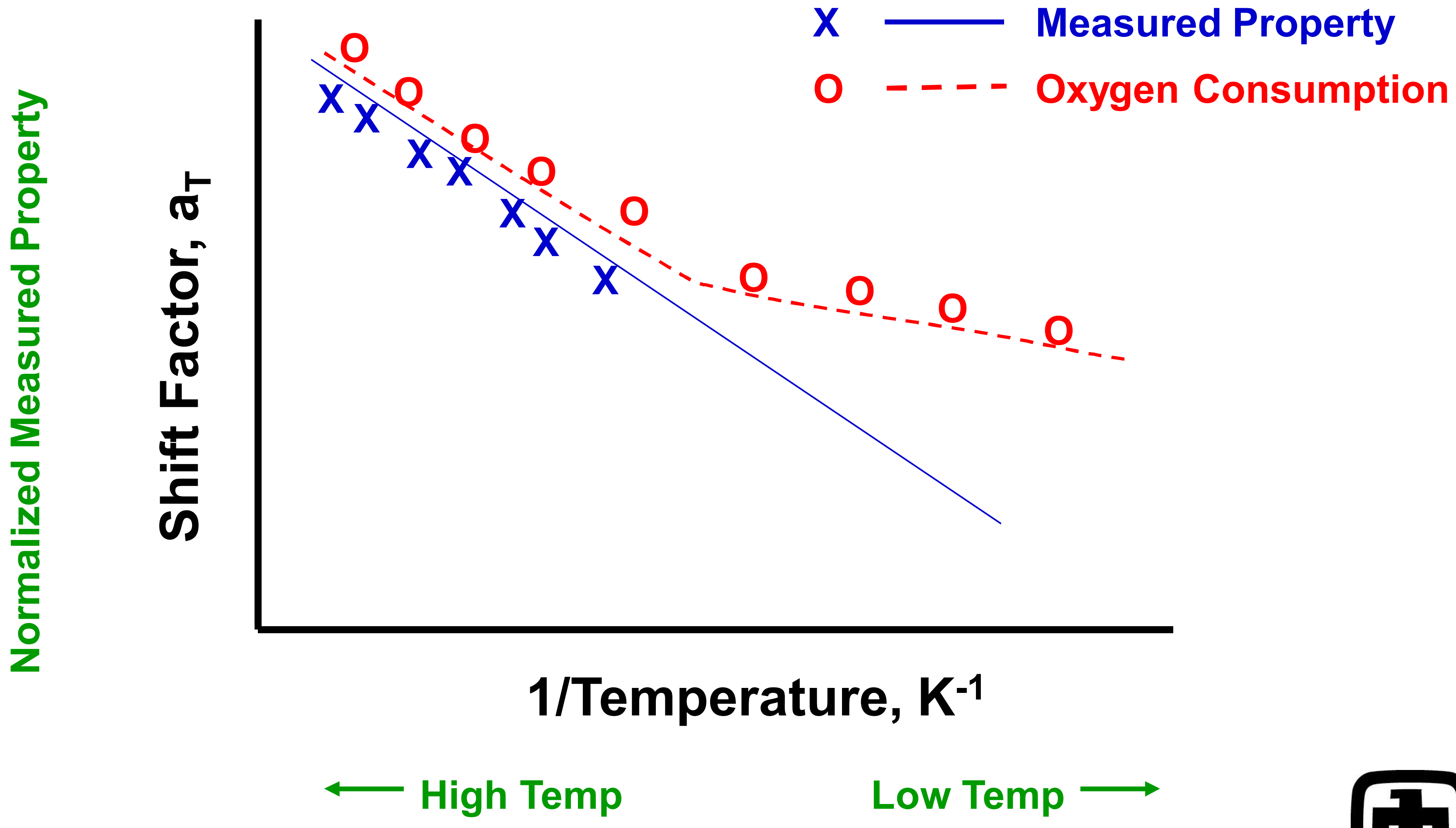


Oxygen Consumption

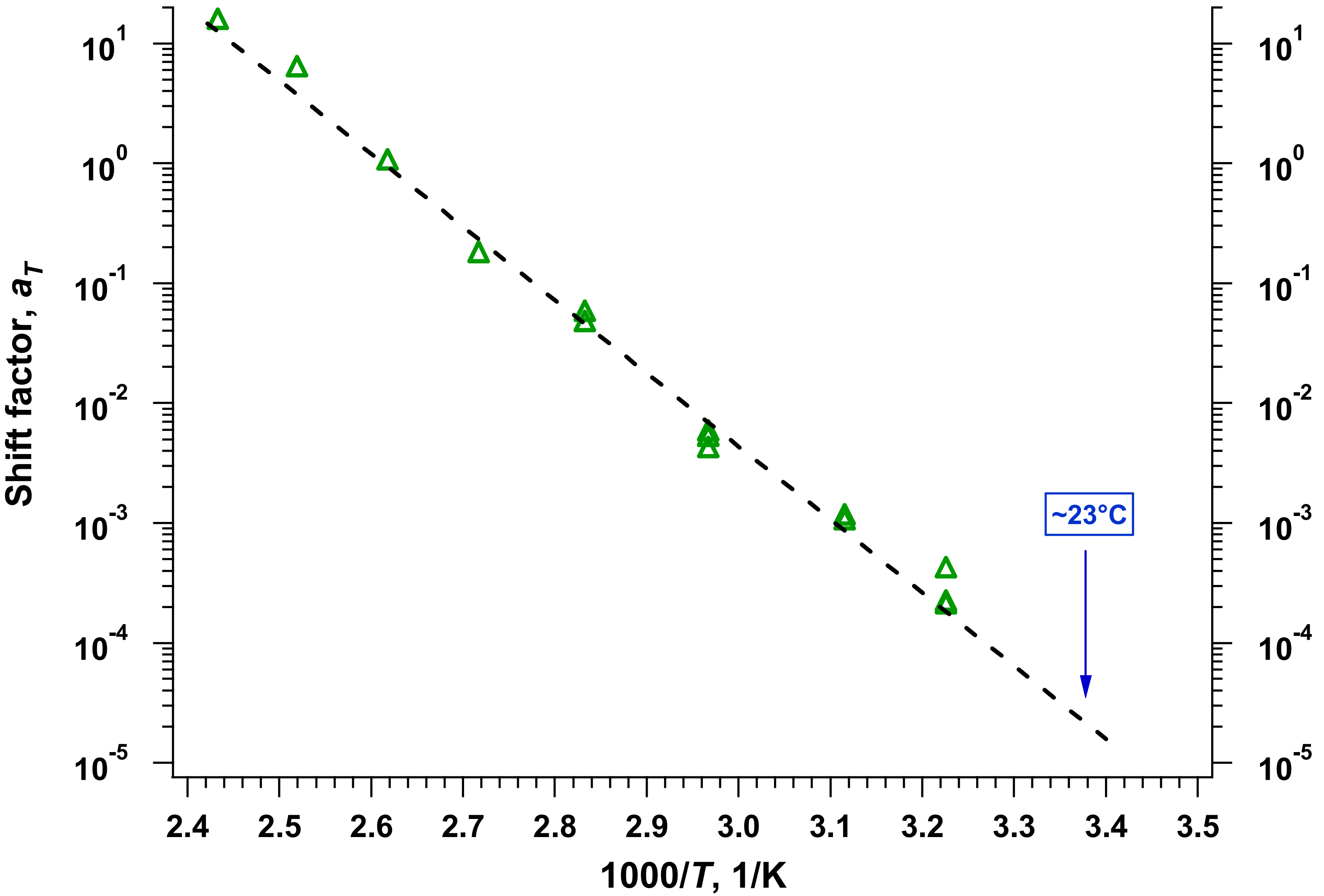
Enhanced Extrapolation ‘Good’



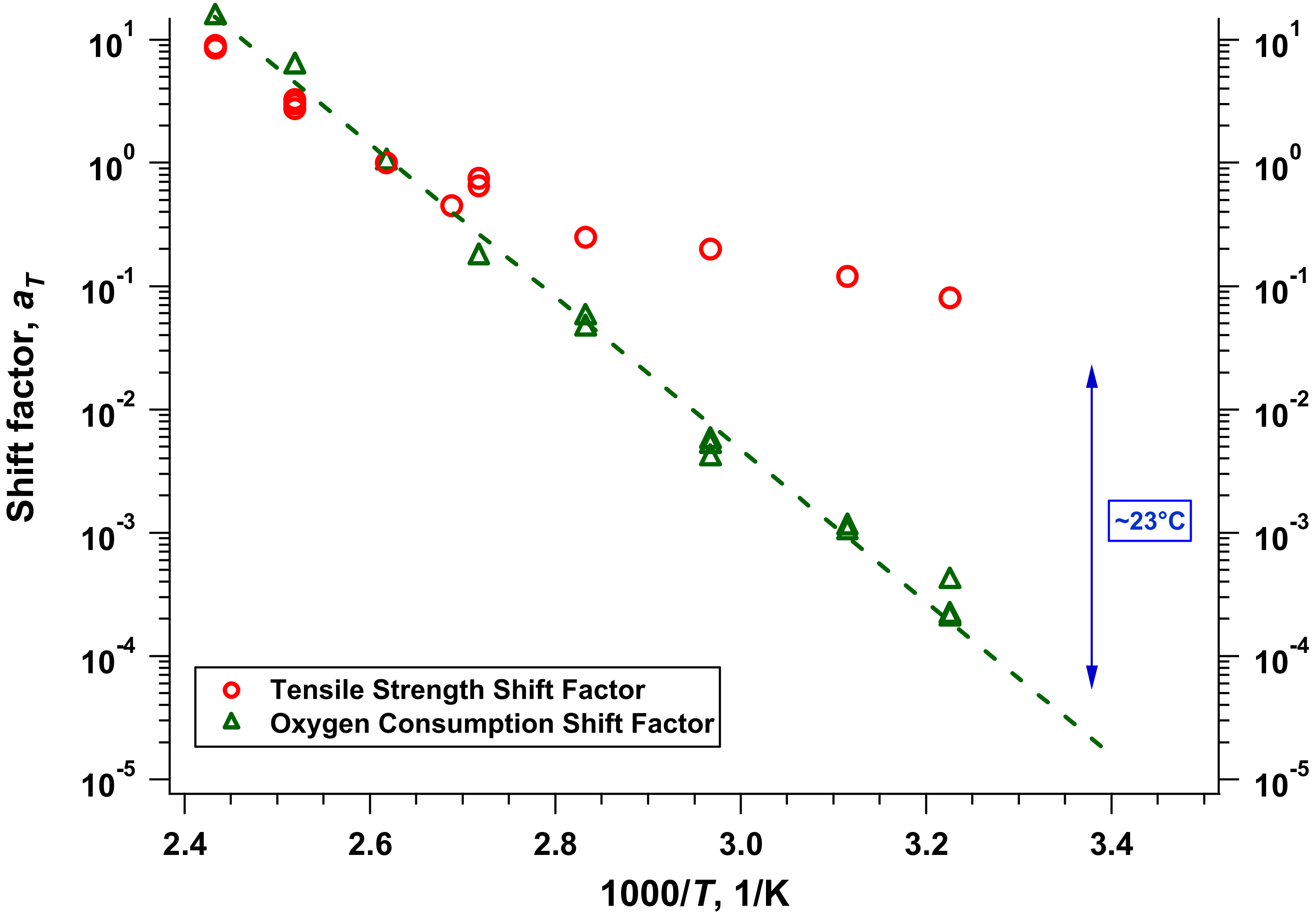
Enhanced Extrapolation: ‘Bad’



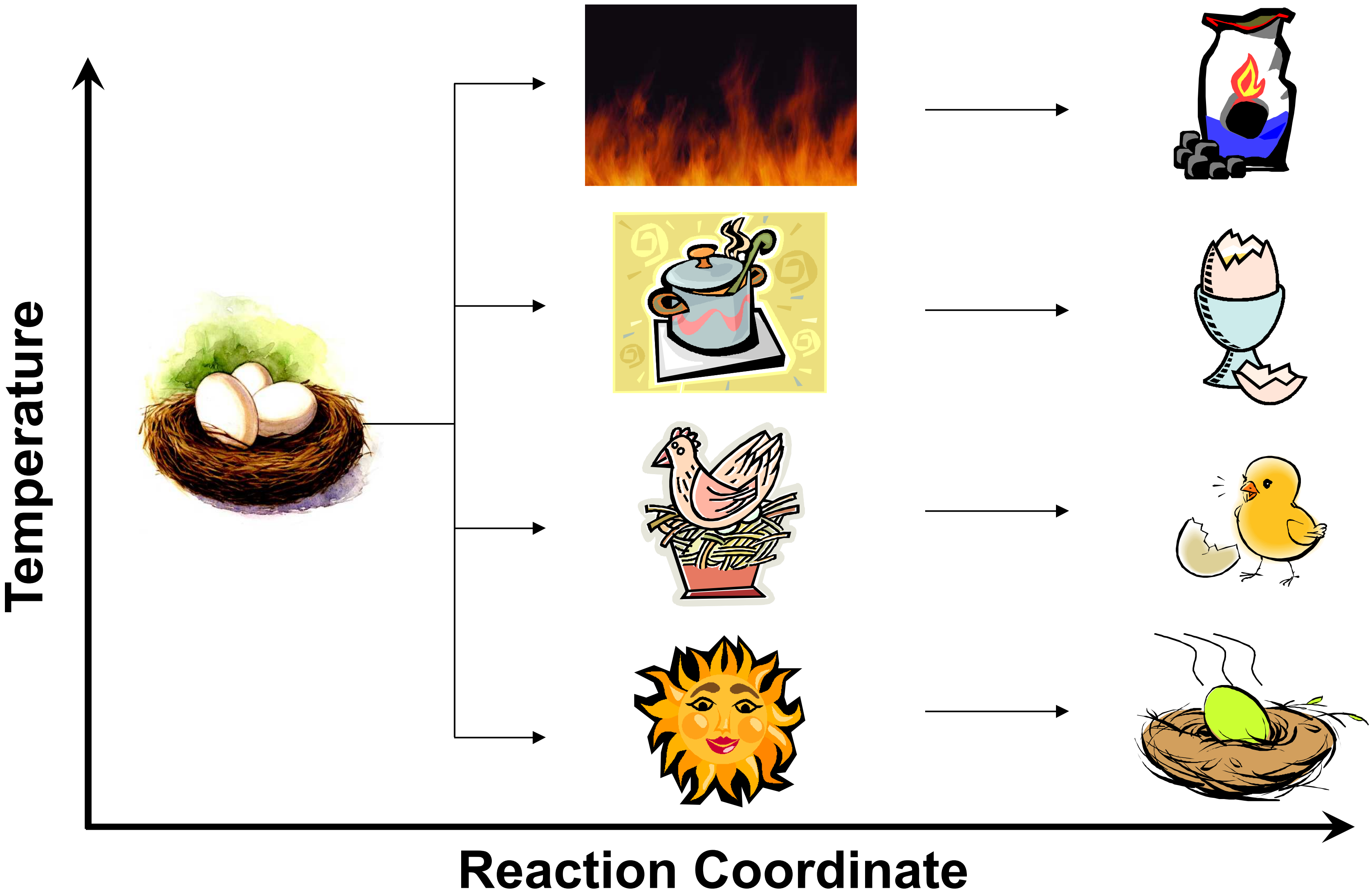
Nylon Oxygen Consumption: Shift Factor Plot



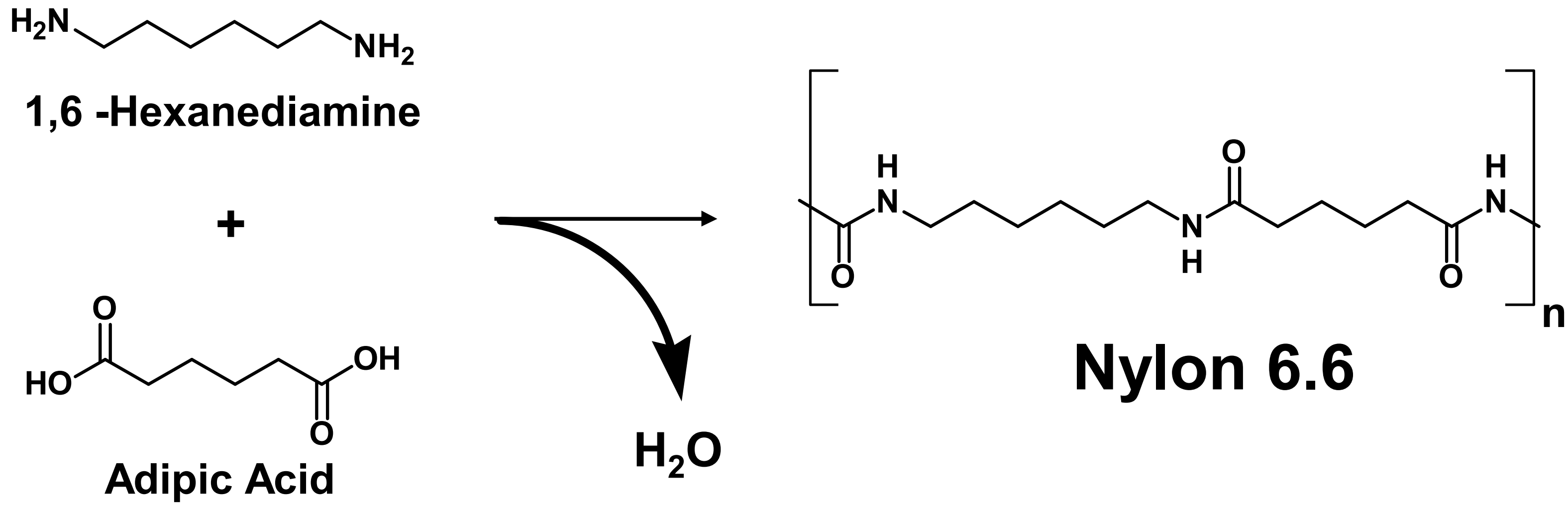
Nylon: Tensile versus Oxygen Consumption

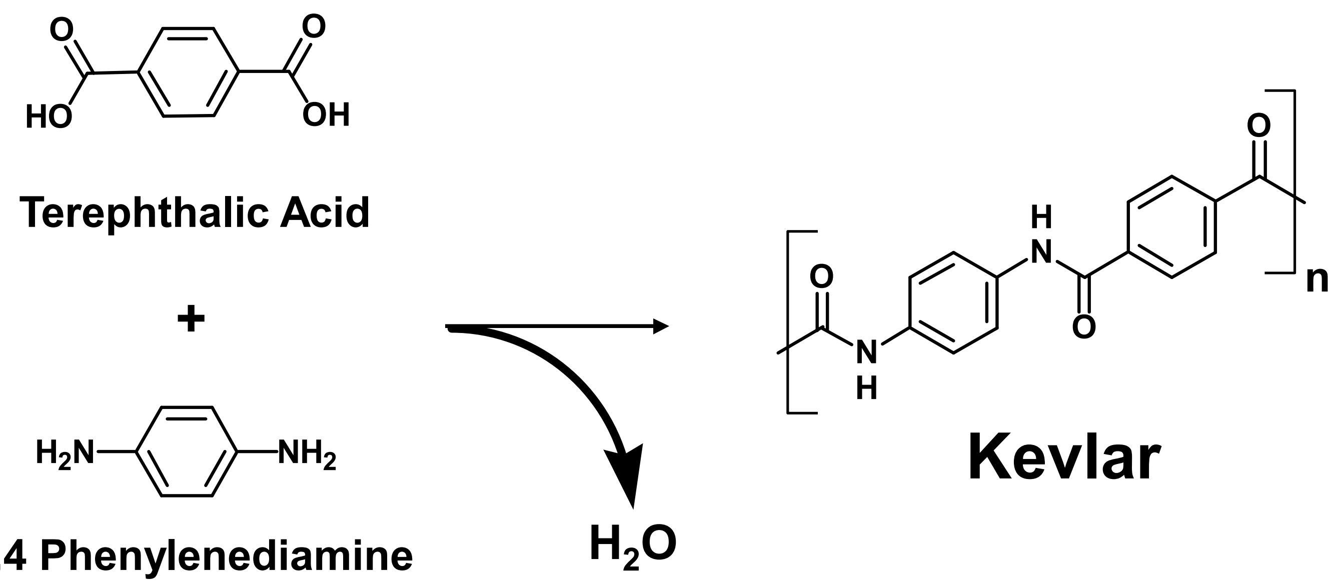


‘Accelerated Aging’



Nylon vs. Kevlar: Aliphatic vs. Aromatic

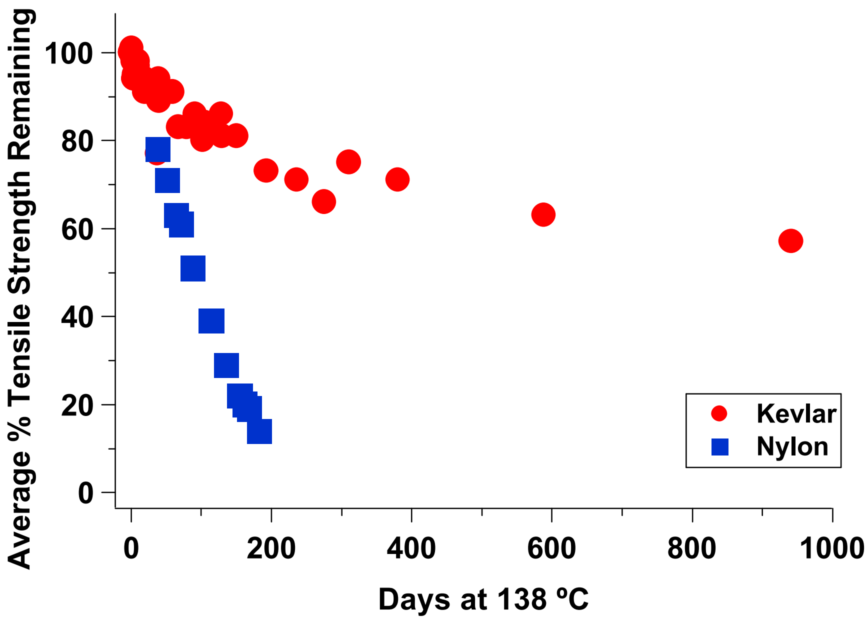




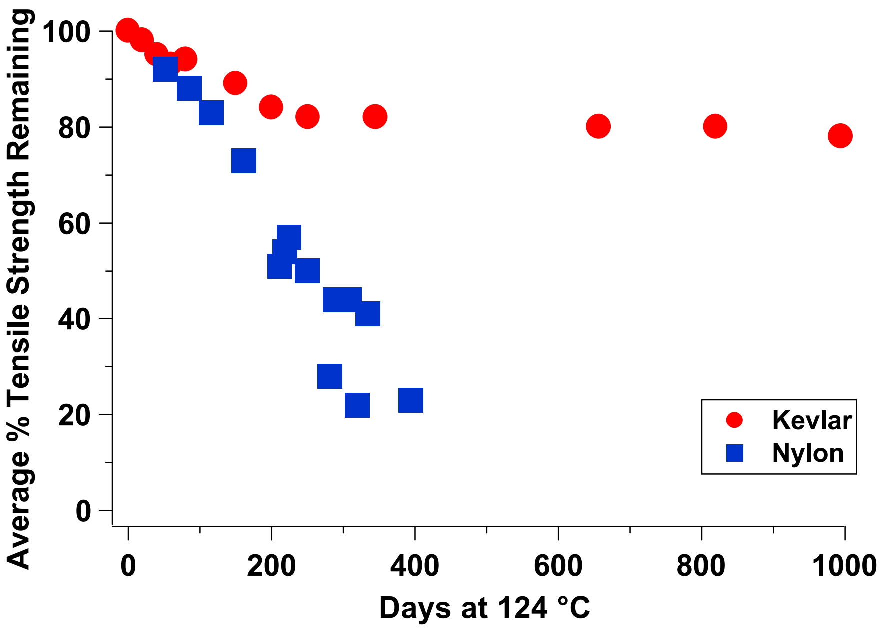
Kevlar vs. Nylon: Thermal-Oxidative Degradation

Polymer + O_2 ⟶ Oxidized Polymer

138 °C



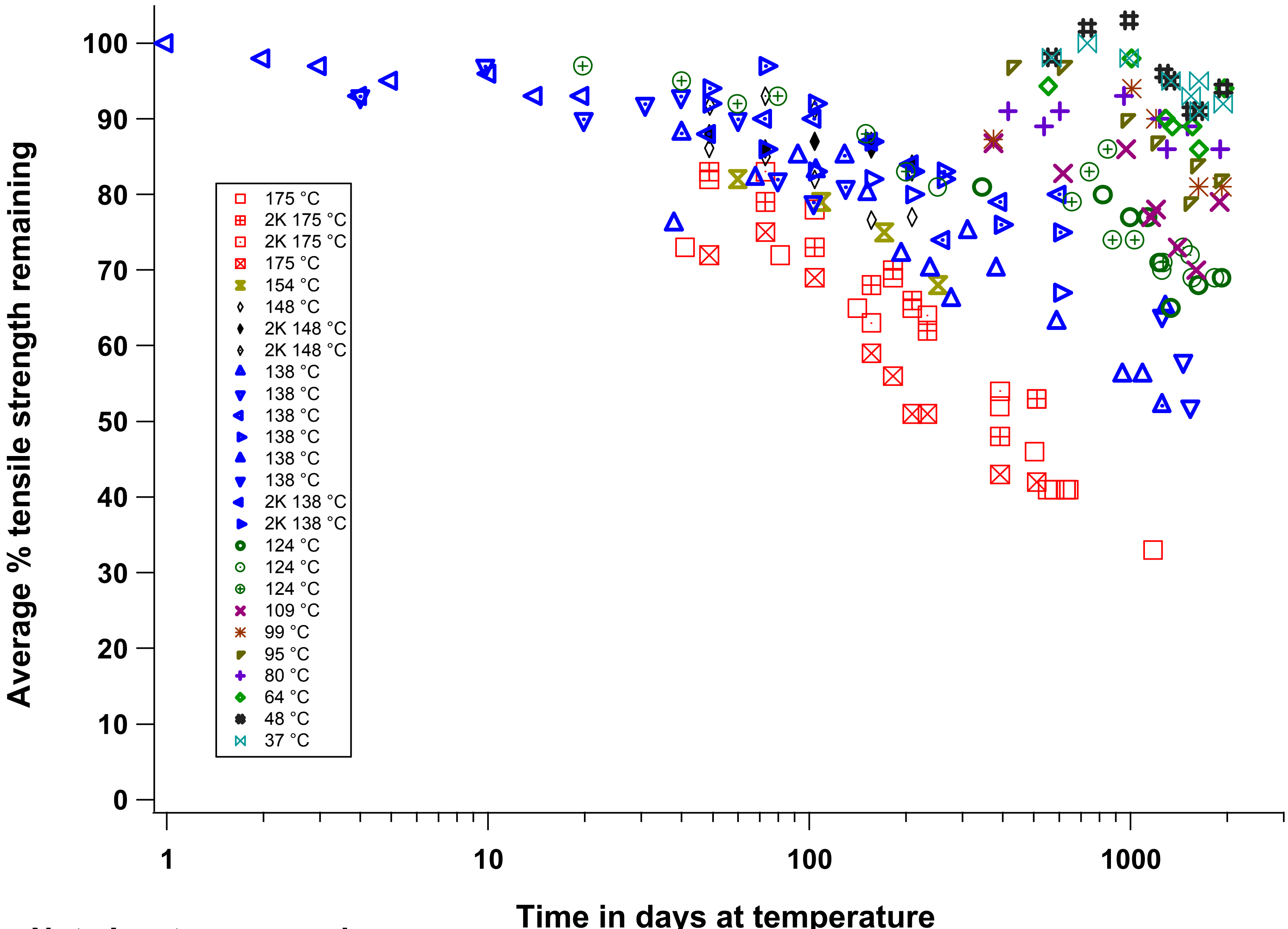
124 °C



Aromatic vs. Aliphatic backbone

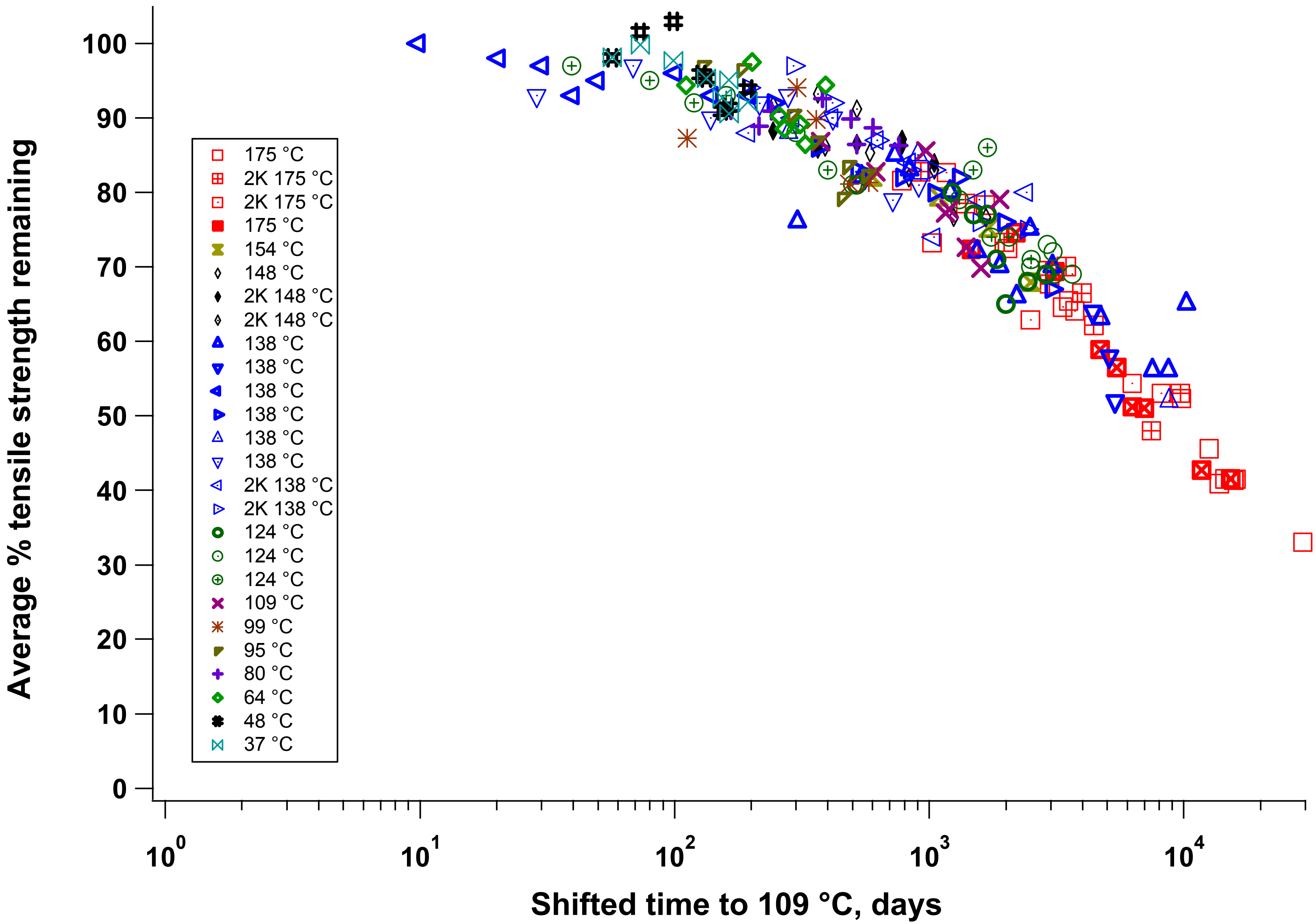
Kevlar more resistant to thermal-oxidative aging than Nylon

Kevlar Thermal oxidative Aging

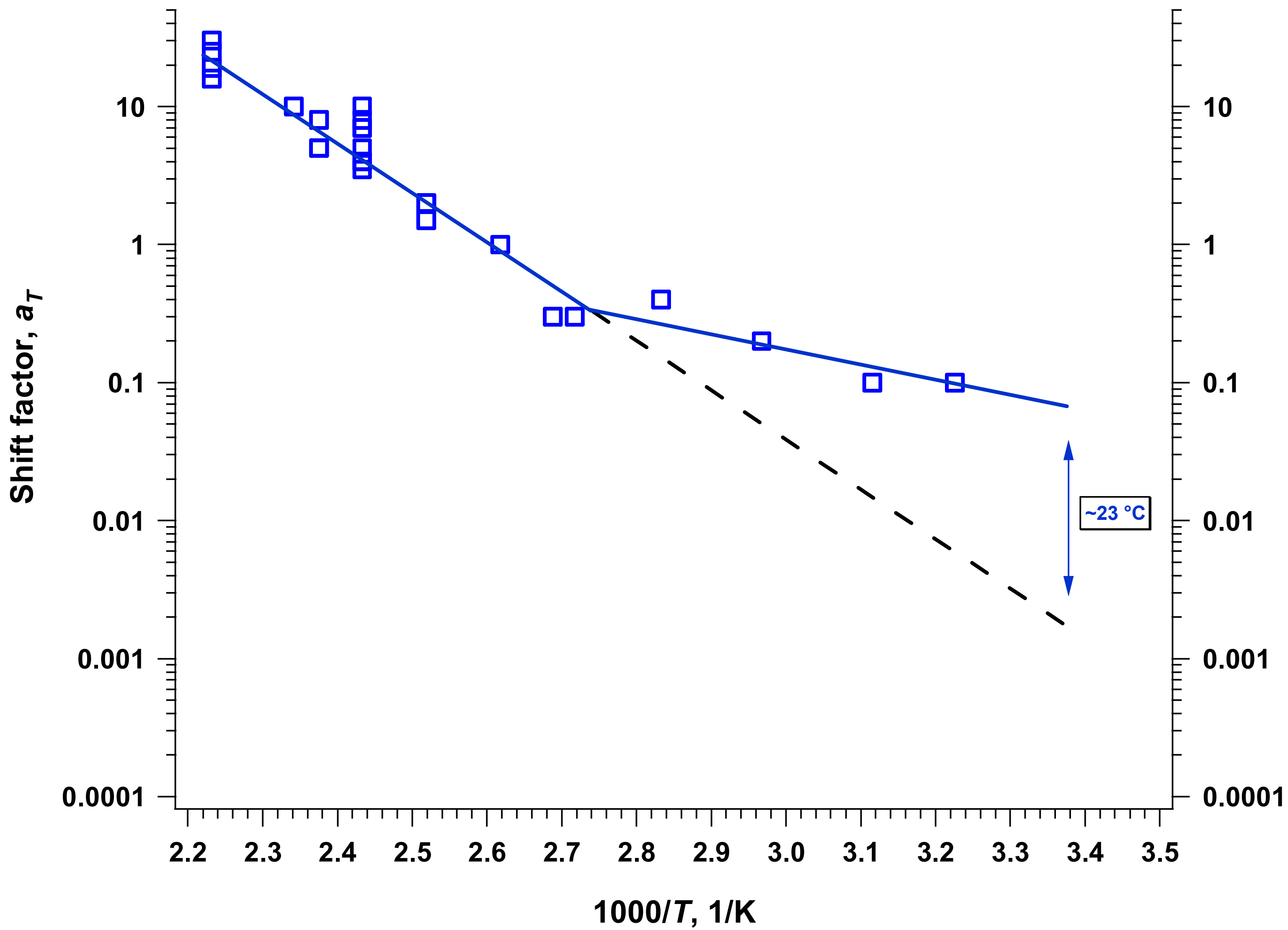


Note low temp crunch….
1K vs. 2K no difference

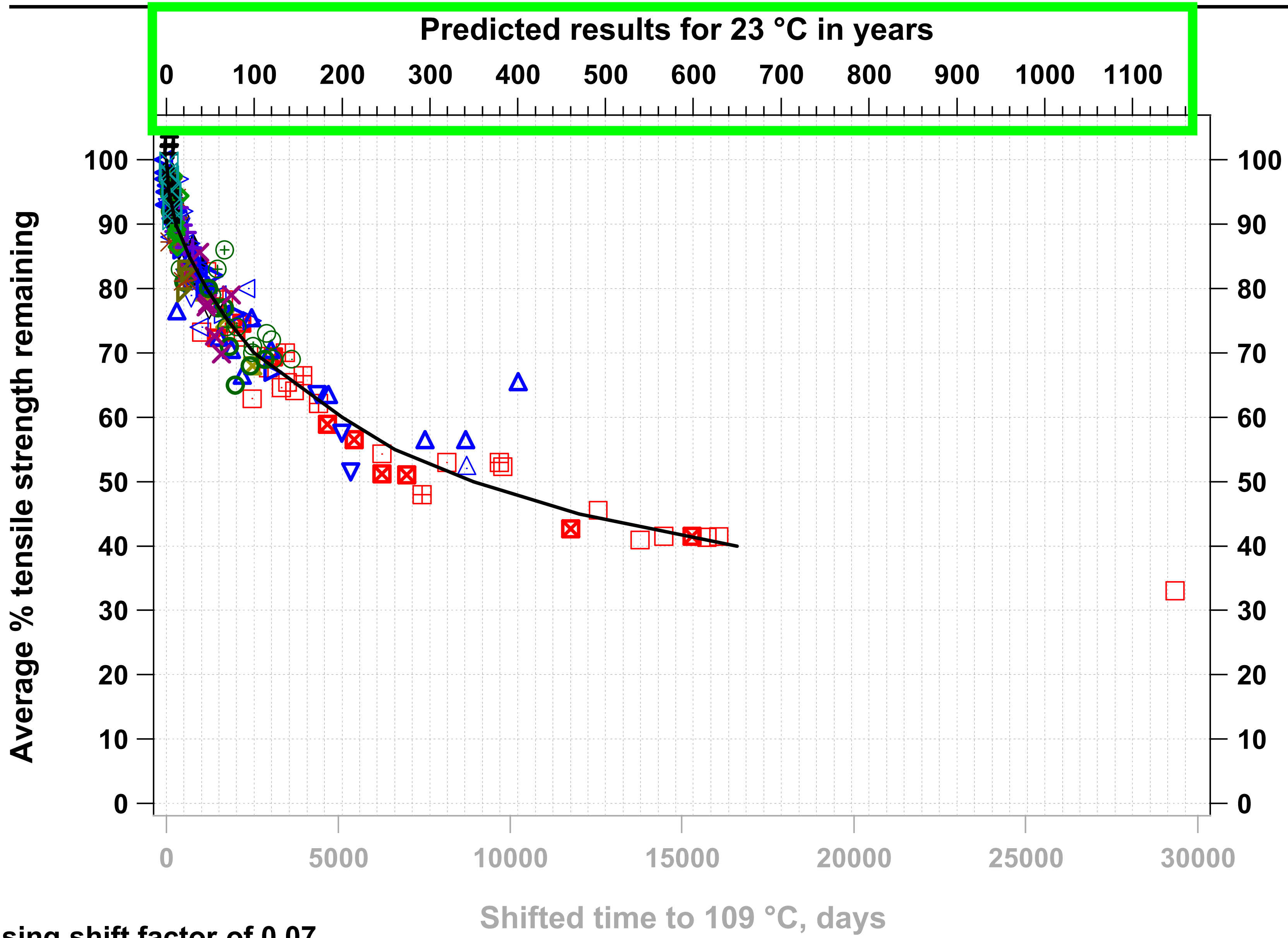
Kevlar Thermal oxidative -Shifted



Kevlar Thermal oxidative –Shifted Factor plot

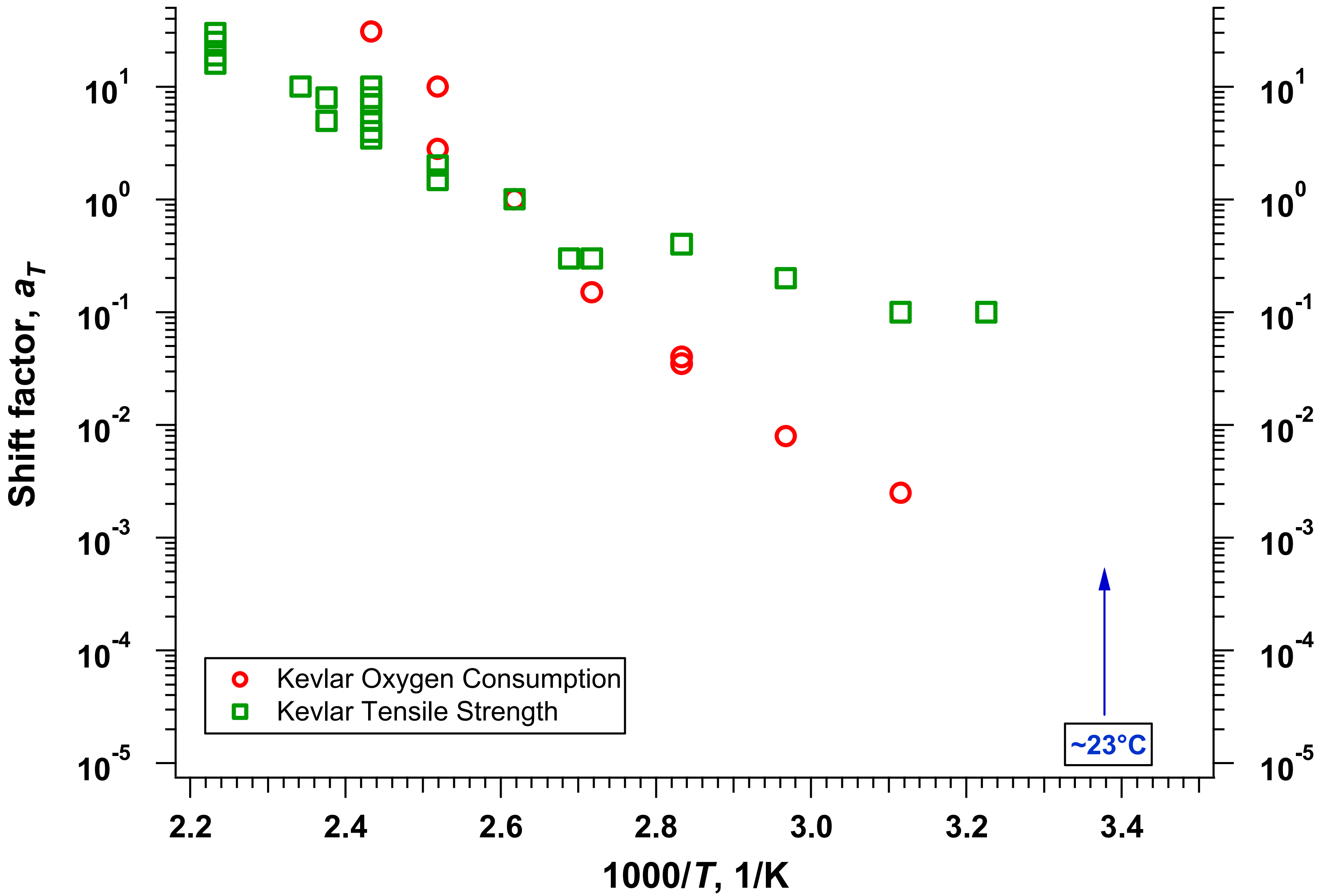


Kevlar Thermal oxidative –RT Prediction

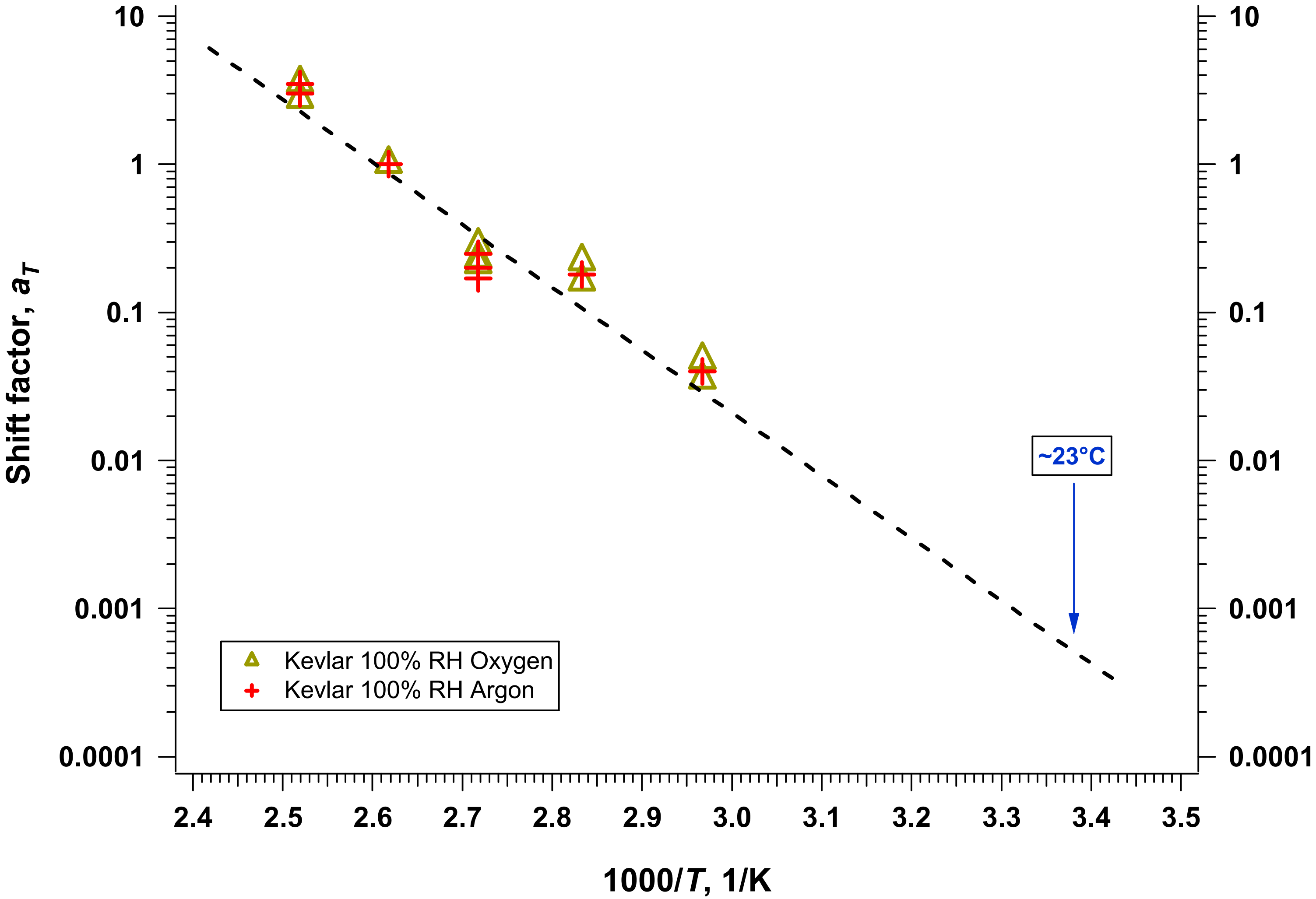


Using shift factor of 0.07

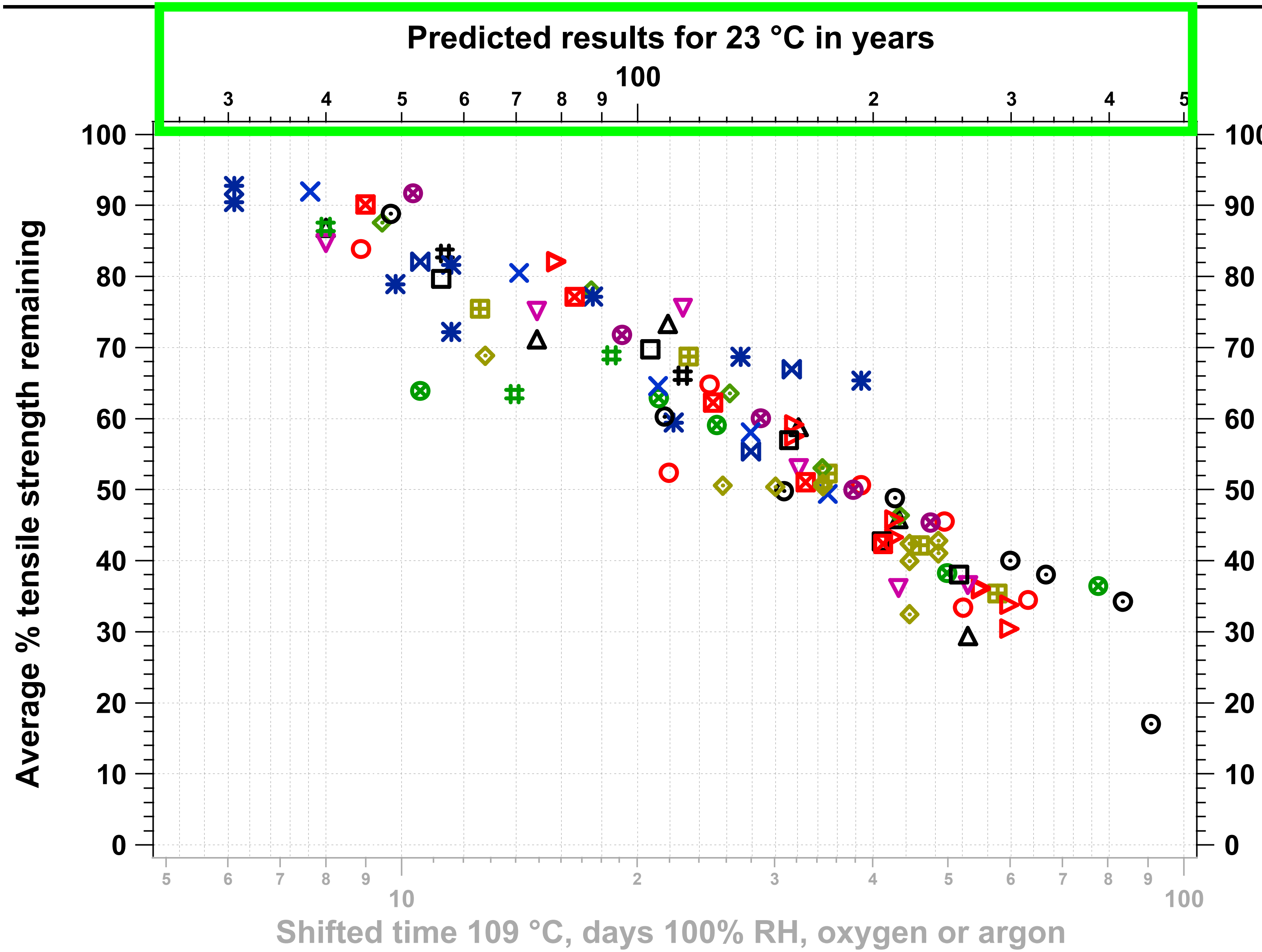
Kevlar Oxygen Consumption vs. Tensile



Kevlar 100% RH Argon and Oxygen –linear fit



Kevlar 100% RH Argon and Oxygen



Conclusions

Nylon linear oxygen consumption

Nylon significant curvature in tensile

Nylon humidity not relevant at lower temperatures
-High temperature data was deceiving

Kevlar has much better aging characteristics but also has significant curvature in tensile

Acknowledgements

-DOE $$$$$

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.

Shift Factors Nylon 100% RH