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The complexity of meaningful and innovative accelerated aging studies: From the crude past to the nano-challenges of today

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Our challenge: Better materials through knowledge of basic performance features and degradation trends

Sandia National Laboratories

South-Western United States

Las Vegas
Albuquerque
Grand Canyon

- Dry semi-desert, but lots of science
- Nuclear, electronics, nano-technology

Sandia National Laboratories Albuquerque-New Mexico

Large US National Laboratory, ~8000 employees
Three traditional defense/energy labs: Lawrence Livermore (CA), Los Alamos and Sandia National Laboratory SNL (NM)

Polymer Performance, Degradation and Materials Optimization

Environmental Polymer Degradation

Degradable Polymer Biomaterials

Controlled Drug Delivery

Service Life Prediction

Polymer Degradation Modeling

Materials Degradation Mechanisms

Polymer Thermal Degradation

Degradation Characterization Analytical techniques

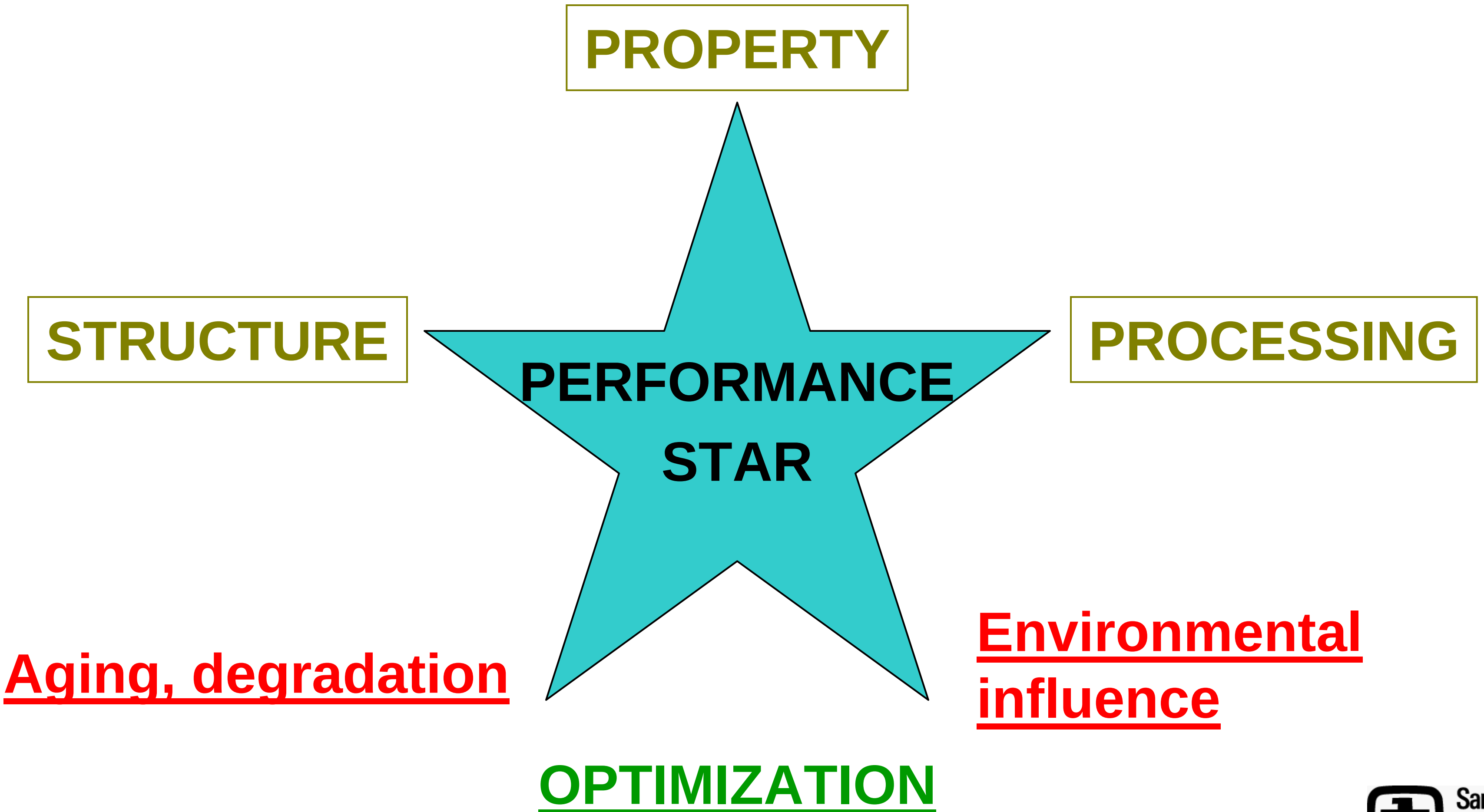
New Materials

Polymer Photodegradation

Polymer Performance:
A research field that is *degrading* into numerous sub-areas
- our research interests are expanding!

High performance polymer materials

- **Know chemical and mechanical properties, processing variables**
- **Select compromise material with optimized desirable properties**



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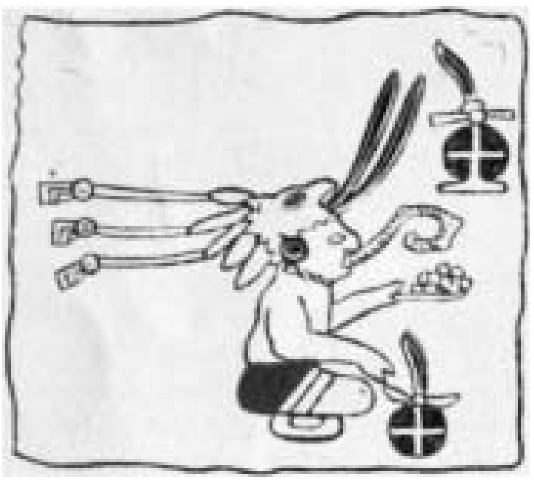
Performance needs of natural rubber many centuries ago

Rubber, when sealed off from light and air lasts very long



Wooden objects with rubber additions made 8 centuries ago

6th-century mural featuring two rubber balls, Aztecs

More than 250 years have passed since rubber was first introduced in Europe. Natives in central America used rubber for various purposes prior to this

Like many other polymers, elastomers will chemically age

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Performance needs of natural rubber many centuries ago

• In 1850 rubber springs were used for simple wagons.

• A railway viaduct in Melbourne uses 12 mm thick rubber blocks in 1889 for support. Today the original NR parts are still functioning. An inspection and analysis of the rubber in 1963 showed a perfect condition.

• In London some buildings (Bishopsgate/Liverpoolstreet station and Victoria Station building) are built on rubber blocks. The largest dimensions of the used blocks are 1200 mm by 1000 mm.

•These early applications are important as it has been possible to closely monitor the behavior of the bearings installed under the Pelham Bridge in Lincoln.

• The inside of a full natural rubber bearing that had been in service for about one hundred years was a little bit stiffer than it was originally but with little change in functionality.

•Taking apart a bearing that was used for about 25 years and measuring the hardness from the outside to the inner side showed that the stiffening of the rubber was limited to a depth of less then 5 mm.

What do we learn? Materials age differently as a function of depth. Macro-heterogeneity and micro-heterogeneity

Basic lifetime prediction

Superposition of exposure times often used for predictions

Age, expose, observe, test specimens, prediction based on trends

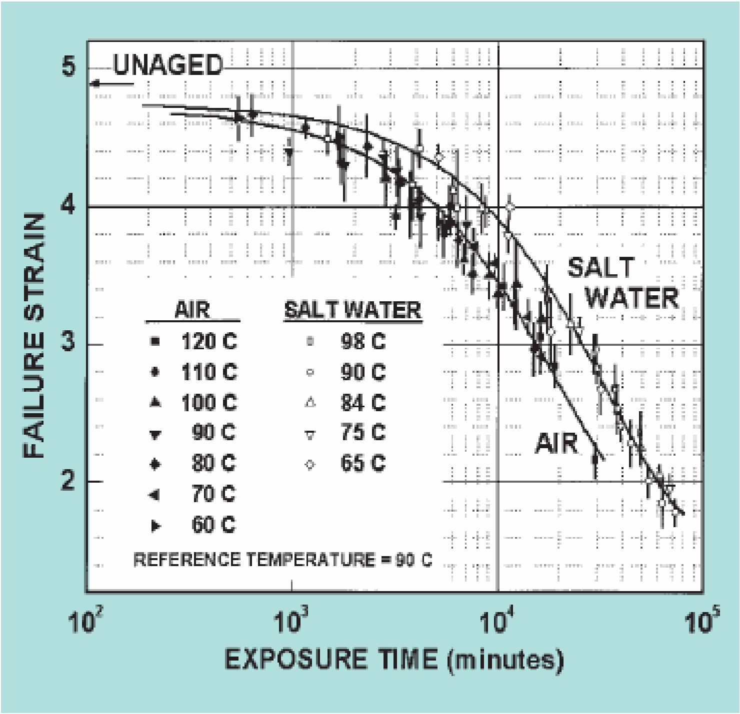

Figure 1. "Master" ageing curves for air and seawater

From NatuurRubber 36, 2004

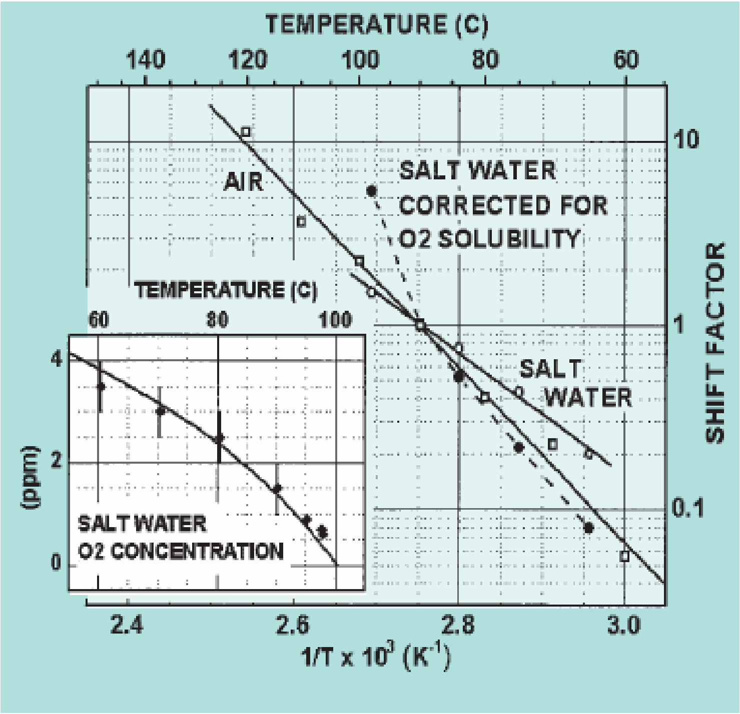

Figure 2. Shift factors used to construct the master curves in Figure 1. The fit lines yield E_a = 90 and 63 kJ/mol for air and seawater, respectively. The dashed curve is the seawater data with the temperature dependence of oxygen solubility. Inset: Measured oxygen solubility for seawater, along with calculated values.

Problem: Costly long term experiments, unreliable short term tests

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Lifetime prediction of polymers

Different ways to understand and describe performance

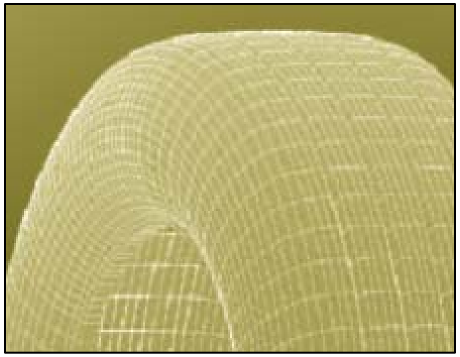
Aging, Degradation

Physical changes

Stress Relaxation

Time dependent constitutive models
FEA modeling

Mechanical properties
Fatigue and stress/strain exposure
Brostow/Corneliussen book



Chemical changes

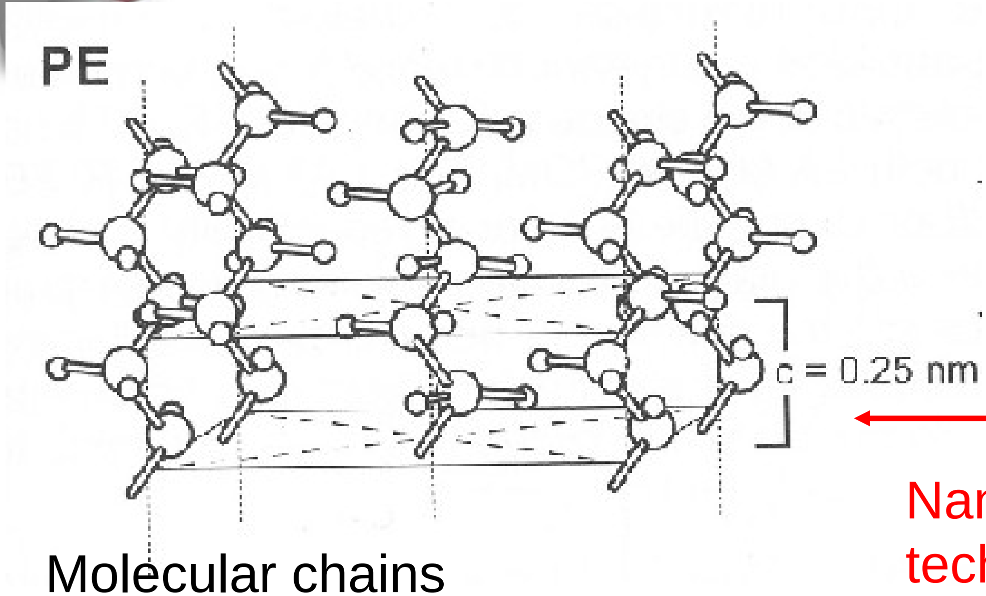
Oxidation, hydrolysis,
other reactions, Mw changes

Polymer science
Materials characterization

Journal: Polymer Degradation and Stability

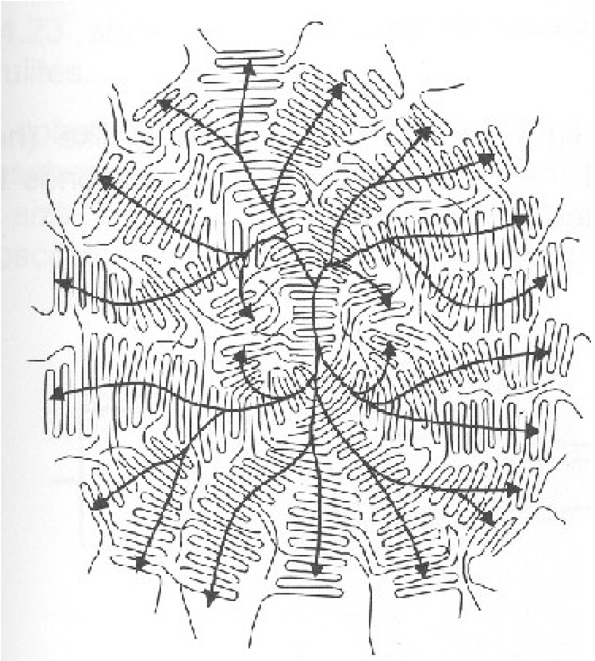
RH, R*, O2, Mw,
scission + crosslinking

Morphological considerations

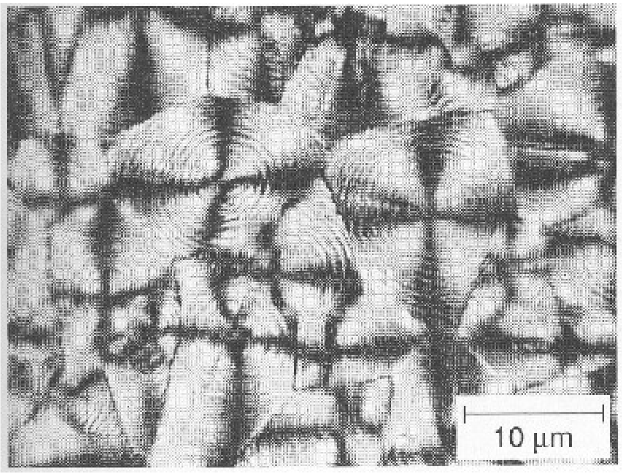


Molecular chains

Nano-
technology



Molecular conformation



Bulk morphology

As materials have complex micro-structure, degradation and performance will depend on different domain-sizes.

Keyword: Physical heterogeneity

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Advances in Technology

How do today's trends in nano-technology affect polymer performance studies?

Nano-technology and polymers?

Some targets are:

- Non-random polymerization
- Controlled molecular architecture
- Design of supermolecular structures
- Custom hybrid materials
- Increased performance features
- Improved processing

New characterization techniques

Visualization, imaging

- AFM and IFM surface analysis
- NMR imaging, faster acquisition
- Imaging capabilities of SIMS and XPS
- IR mapping and direct surface scans
- Raman microprobes
- Efficient mass-spec analysis
- Coupling of instruments TGA-IR-MS
- Surface responsive detection QMB
- Beam scattering and IR absorption-reflectance spectroscopy

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Dynamic TGA studies for nano-composites

Aim: Use rapid thermal degradation to assess performance

- Variables: Heating rate, conversion (weight loss), activation energy
- Complications: DLO, sample geometry and weight, atmosphere and non-linear degradation processes
- Different models compete

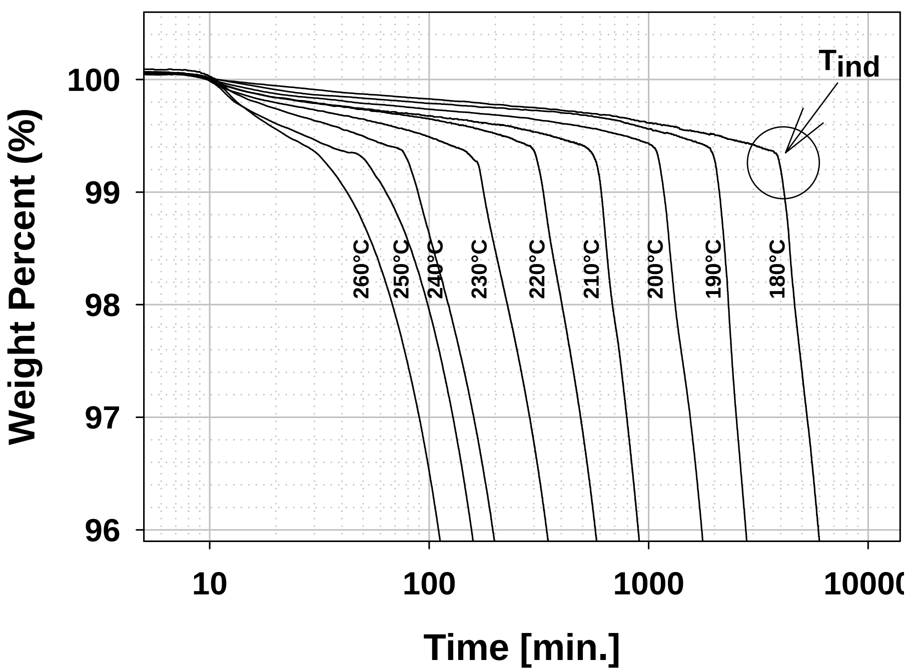
Model	Mathematical relationship	Plots
Friedman	$\ln(d\alpha/dt) = \ln[Af(\alpha)] - E_a/RT$	$\ln(d\alpha/dt)$ vs $1/T$
Kissinger	$\ln(\beta/T_p^2) = \ln(AR/E_a) + (1/T_p)(-E_a/R)$	$\ln(\beta/T_p^2)$ vs $1/T_p$
Flynn-Wall-Ozawa	$\log\beta = \log\frac{AE_a}{Rg(\alpha)} - 2.315 - 0.4567E_a/RT$	$\log\beta$ vs $1/T$
Coats-Redfern (modified)	$\ln\left[\frac{\beta}{T^2(1-2RT/E_a)}\right] = \ln\left[-\frac{AR}{E_a\ln(1-\alpha)}\right] - E_a/RT$	$\ln(\beta/T^2)$ vs $1/T$

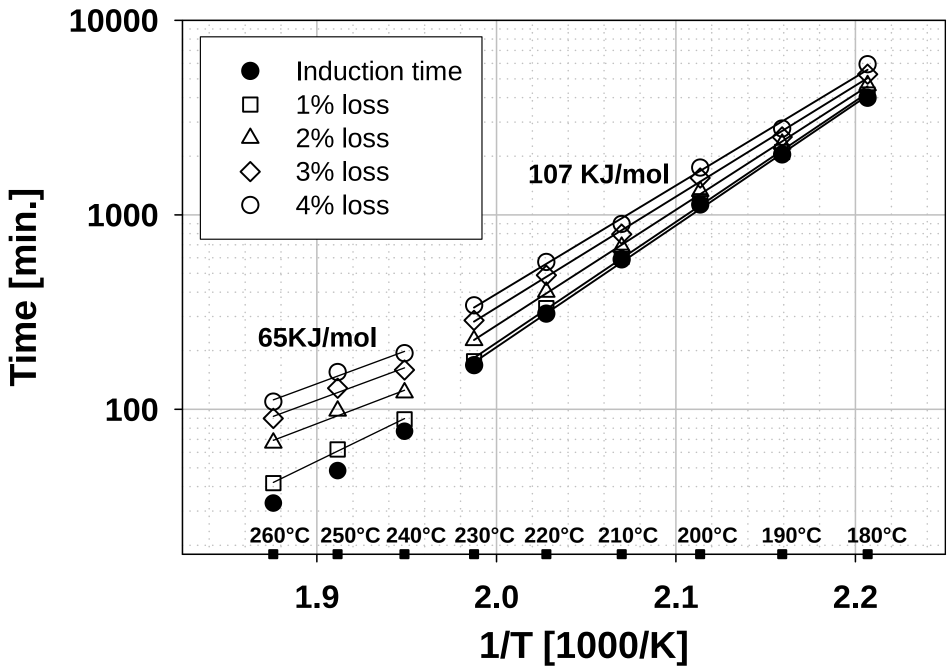
Higher Eact. are often associated with better materials

Experiments are fast but great care is required for meaningful studies

Complexity even in isothermal TGA studies

- Oxygen availability and diffusivity affect thermal degradation at higher T
- Mechanistic changes as a function of temperature
- Example: filled EPR material.





Activation energy depends on temperature

Linear conditions will not always apply, other processes are important

Fast TGA techniques are over-emphasized for performance evaluations

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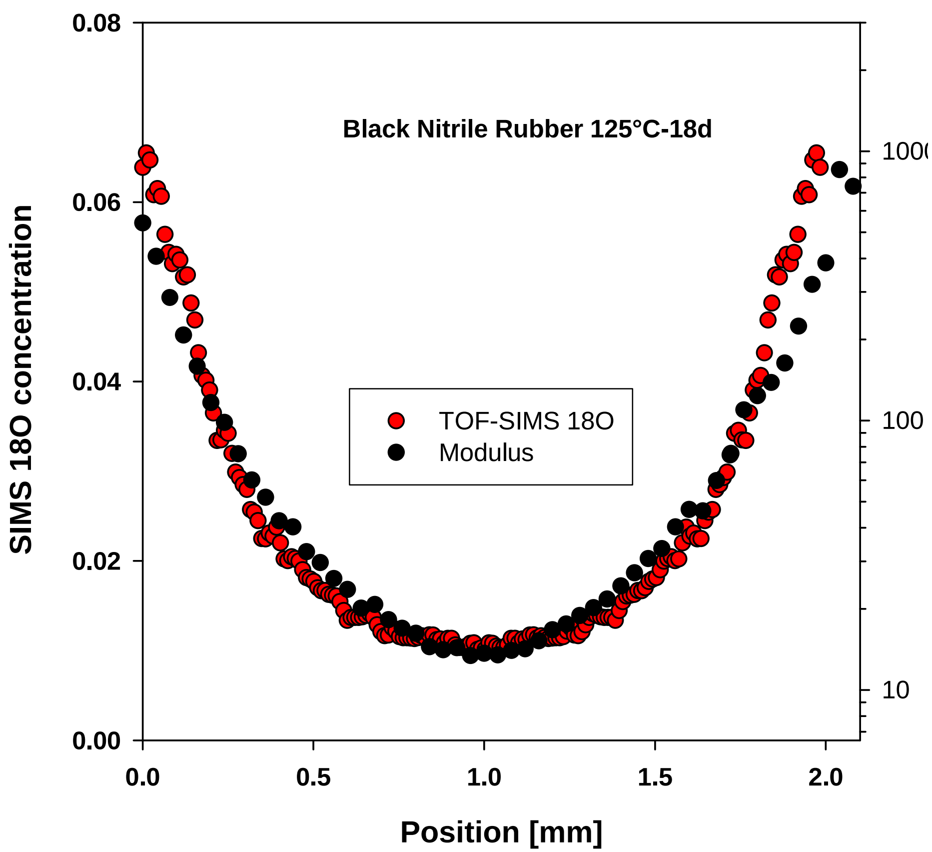
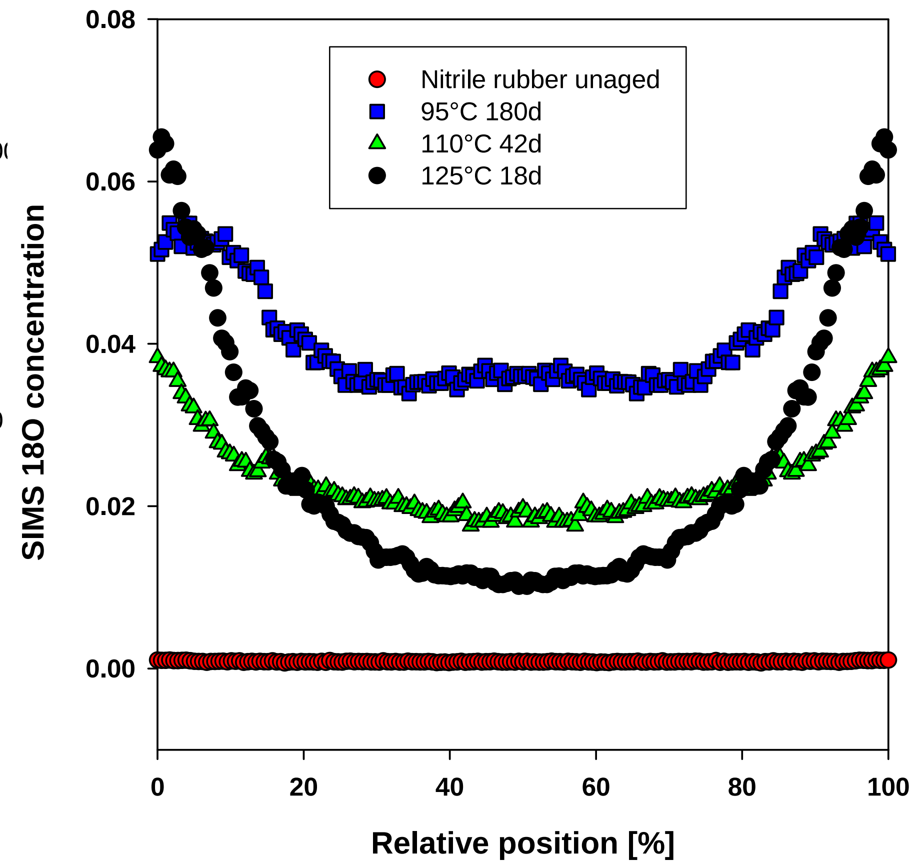
TOF-SIMS scanning approaches for DLO assessments

Example: Fast screening techniques for degradation profiles are needed, important feedback on mechanism

- Used novel TOF-SIMS screening techniques with quantitative feedback
- Isotopic labeling (18O) and direct analysis (16O) are possible

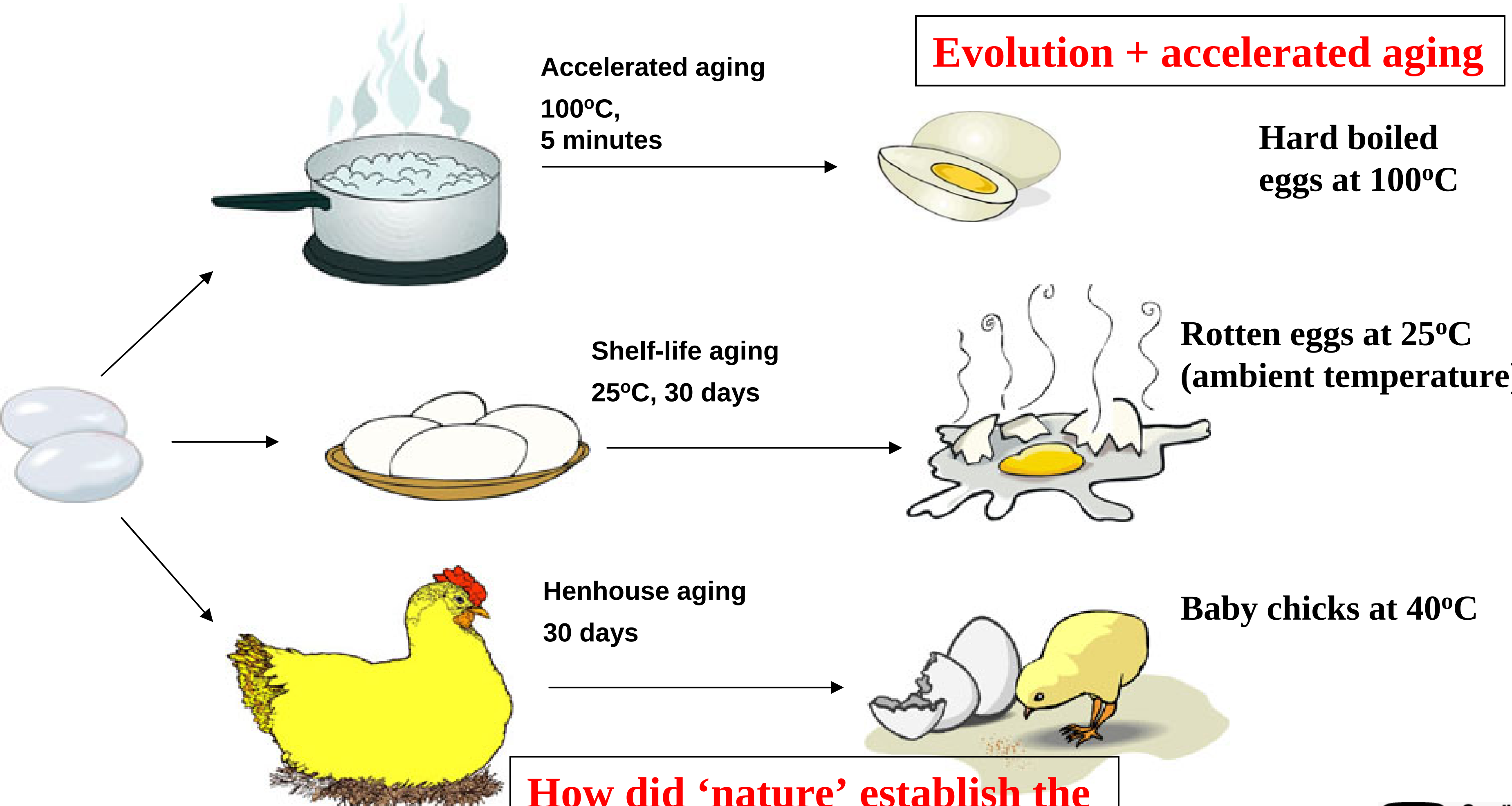




Reactions may change with temperature

- **Two fundamental issues: The classic chicken or the egg problem Plus, temperature conditions for perfect aging, do they exist?**

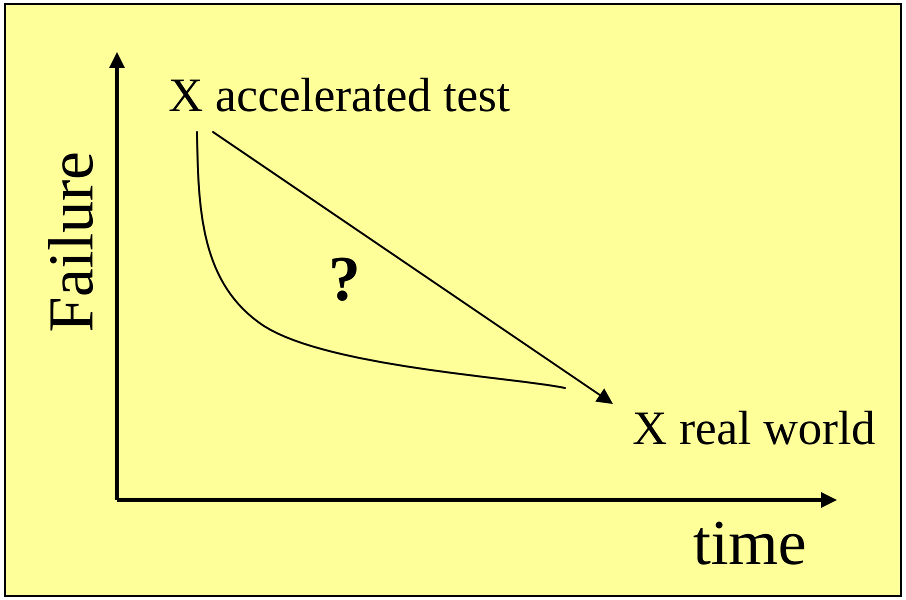
Evolution + accelerated aging



How did 'nature' establish the perfect aging temperature ?

Failure processes - time dependency

- **Infant mortality often controlled by material robustness**
- **Random failure develops with time**
- **Wear out, autocatalytic failure increase and final life**



Common extrapolations:
Arrhenius
Inverse power law
Eyring
WLF

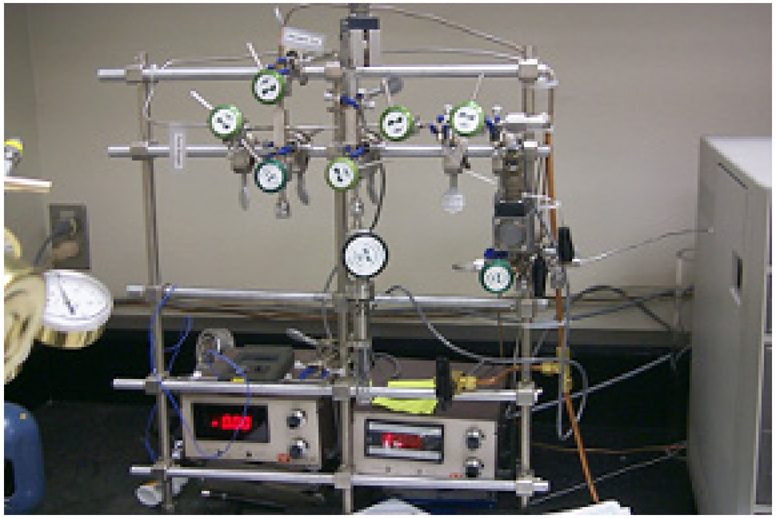
What makes extrapolations difficult?
The usual suspects !!!

Complex materials
Processing variations, additives etc.
Failure modes need to be established
Need to determine acceleration factors
Variability in aging mechanism
Variability in sample to sample
Static versus dynamic aging exposure (just oven exposure or cyclic stresses)

Also: Fundamental anomalies?

Oxygen consumption-Predicting aging at low T's

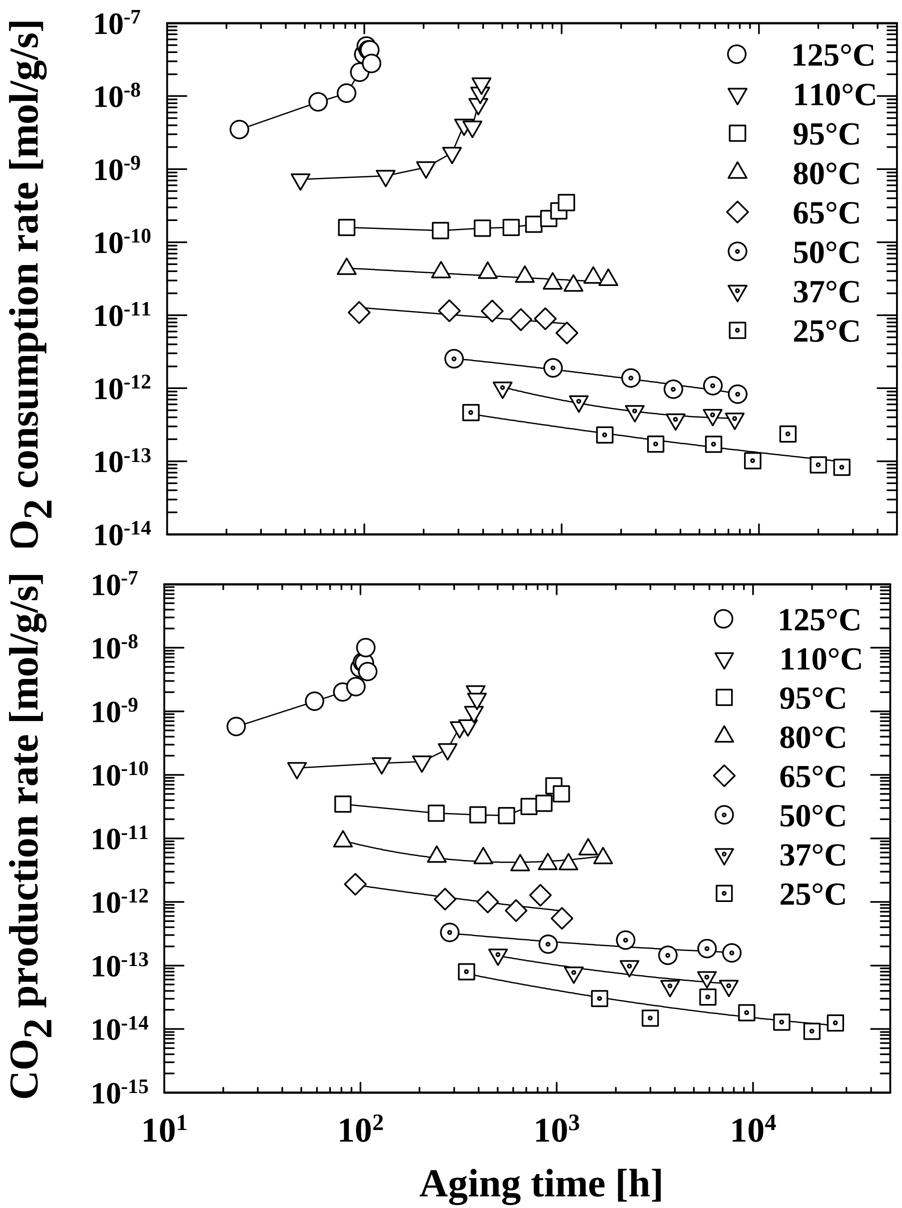
- **Manifold, ampoules, GC-analysis, P transducer**
- **Fill ampoules to P_{O2} required**
- **Determines consumed O_2 and produced CO_2/CO**
- **High dynamic sensitivity, polymer/free gas volume**
- **Measures oxidation rates ranging from 10^{-8} to 10^{-13} mol/g-s**
- **Experiments require days to months at RT**
- **Many polymers consume ~20cc/g STP of O_2 to mechanical failure**
- **10^{-13} mols/g-s equivalent to life-times of ~ 280 years at RT**



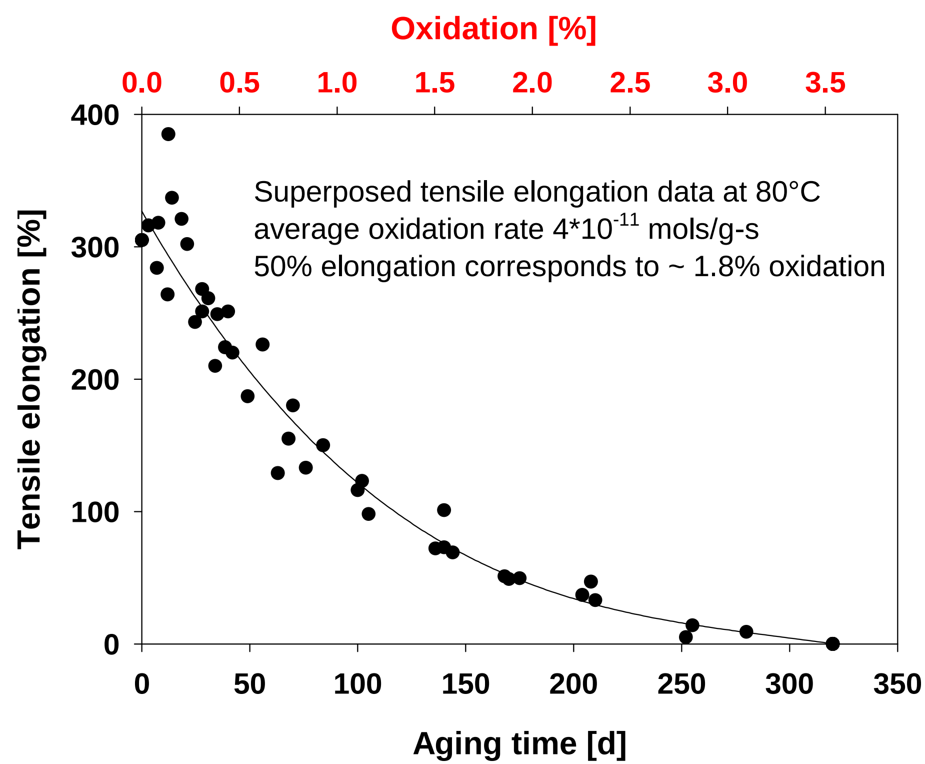
Note: Rates are corrected for increase of P with T, dissolved gas and volatiles

J. Wise, K. Gillen, R. Clough, *Poly. Deg. Stab.*, *4* (1995) 403

Oxygen consumption-Predicting aging at low T's

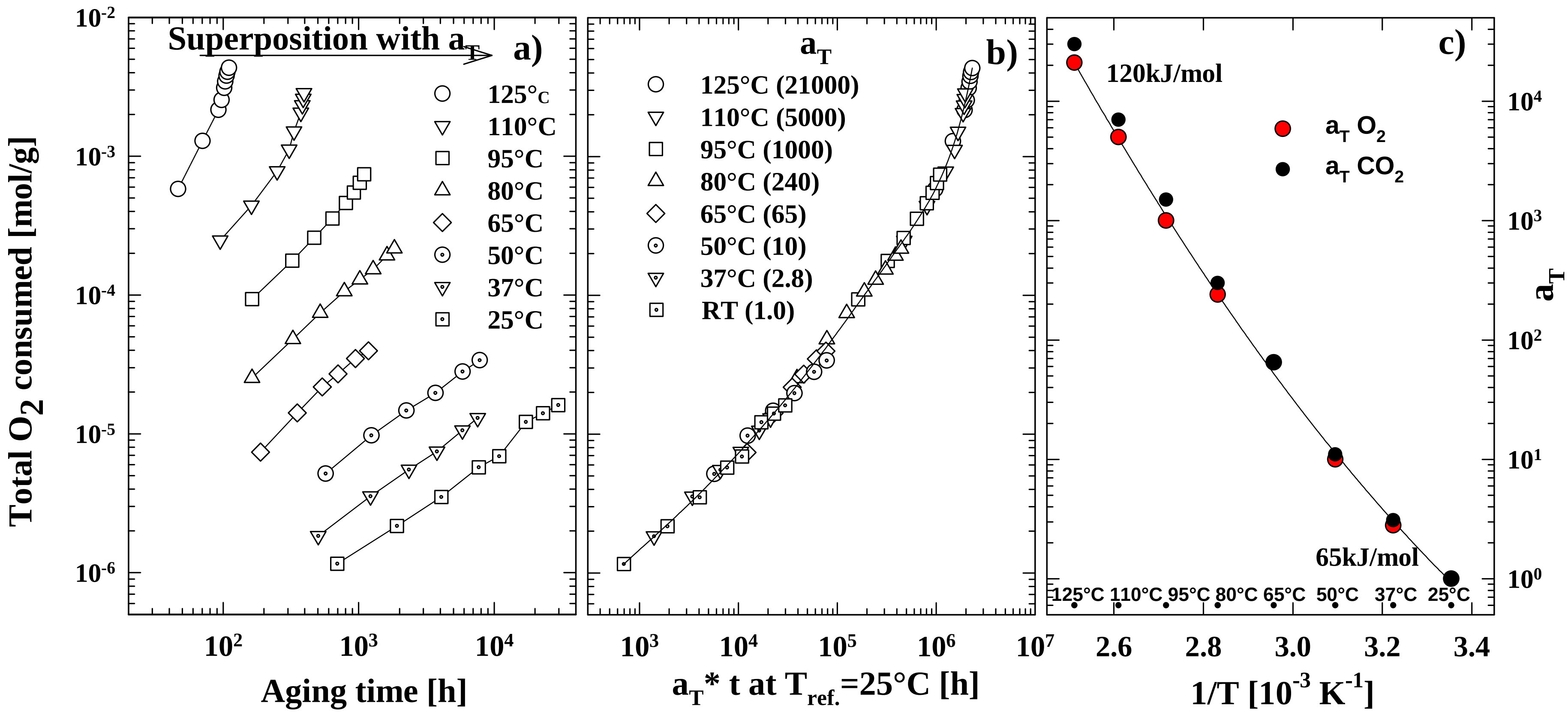


- **Comparison of oxidation rate and CO_2 formation, mechanism feedback**
- **Correlation of oxidation level and mechanical properties, property predictions**



Oxygen consumption-Predicting aging at low T's

- **Time/temperature superposition of oxidation levels in PU elastomer**
- **Curvature in Arrhenius plot (similar for O_2 and CO_2)**
- **Time/temperature superposition for shift factor determination**



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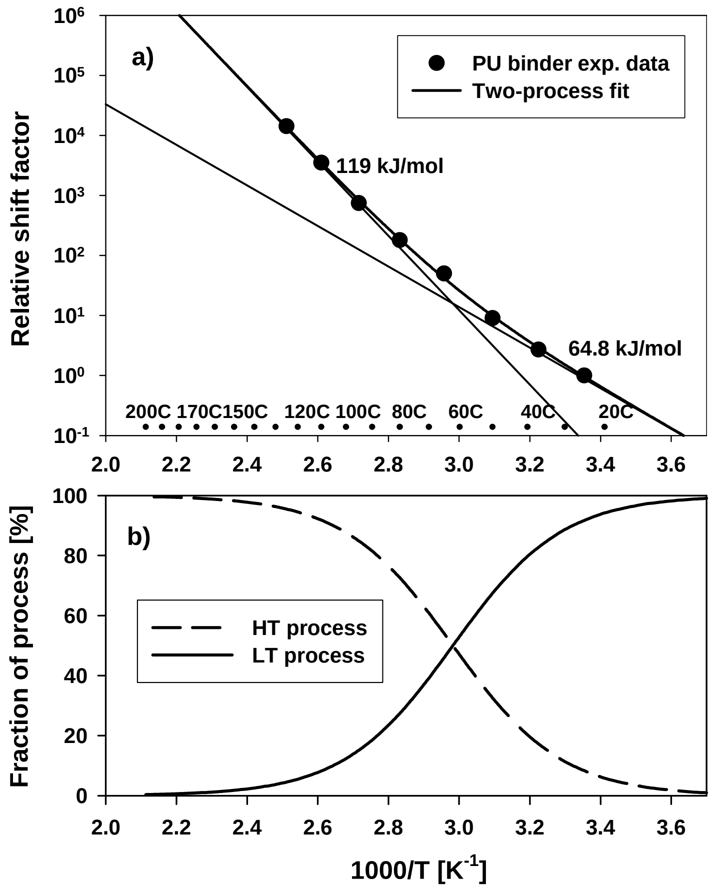
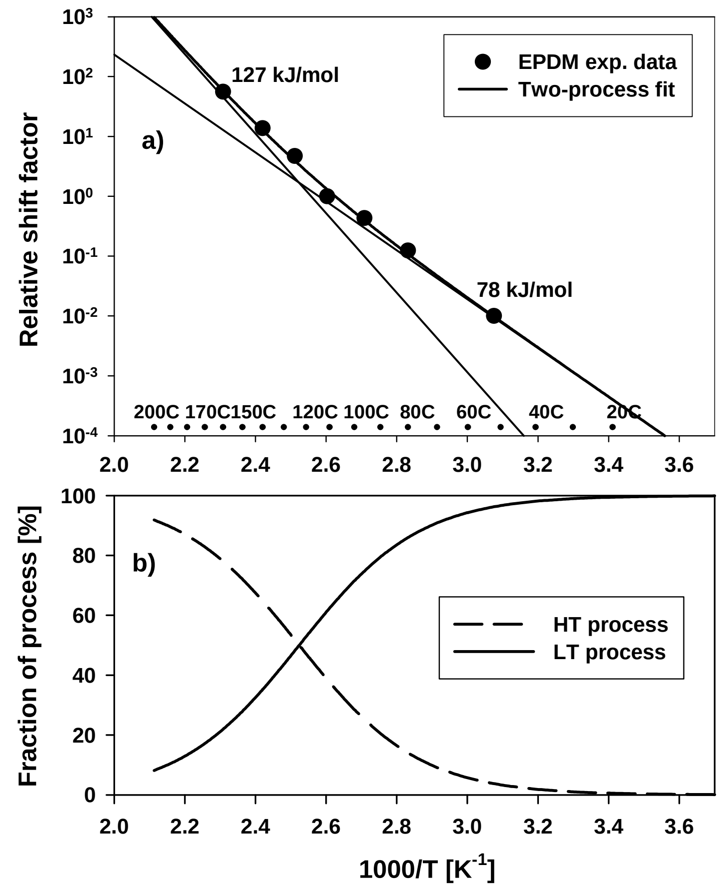
Curvature in Arrhenius plots – mechanistic change with T

- **Evidence for curvature in many materials**
- **Combination of high and low temperature process**
- **Important for lifetime predictions**

$$k_{sum} = k_1 + k_2 = A_1 * \exp(\frac{E_{a1}}{RT}) + A_2 * \exp(\frac{E_{a2}}{RT})$$





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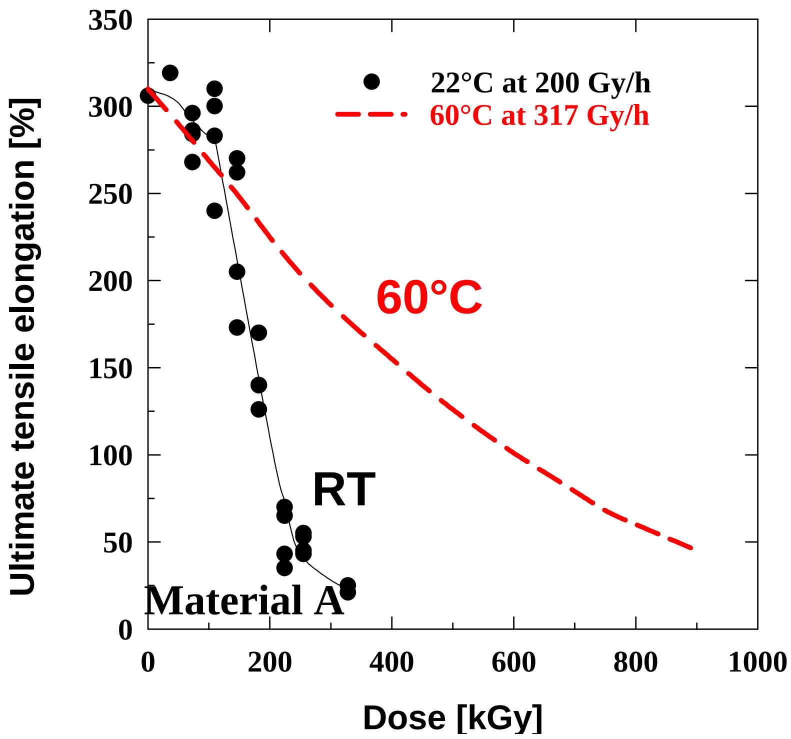
M. Celina, K. Gillen, R. Assink, *Poly. Deg. Stab., 90* (2005) 395

Anomalous aging effects

- Anomalous aging effect in temperature-radiation environments
- Observed for various crosslinked polyolefin materials (cable insulation)
- Reflects mechanistic variations in degradation mechanism
- Elevated temp aging could not predict low temp degradation

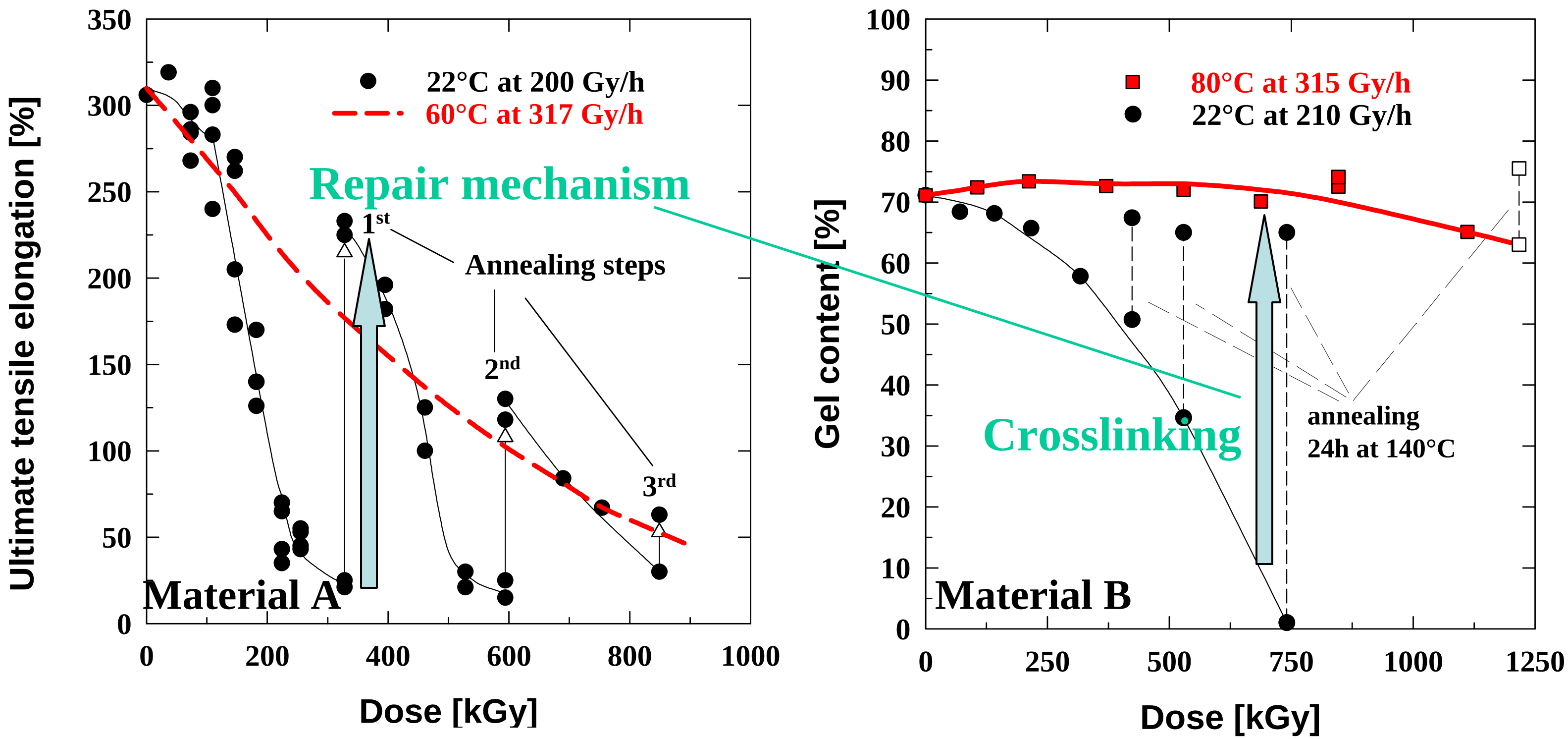


- Radiation + thermal aging
- Oxidative conditions, different to space but shows how unexpectedly materials may behave

M. Celina, K. Gillen, J. Wise, R. Clough, *Radiat. Phys. Chem., 48* (1996) 613
M. Celina, K. Gillen, R. Clough, *Poly. Deg. Stab., 61* (1998) 231

Anomalous aging effects

- Anomalous aging effect in temperature-radiation environments
- Observed for various crosslinked polyolefin materials (cable insulation)
- Reflects mechanistic variations in degradation mechanism
- Elevated temp aging could not predict low temp degradation
- Competition between scission and crosslinking (only active at high T's)
- Faster aging at lower temperature (only scission)



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M. Celina, K. Gillen, R. Clough, *Poly. Deg. Stab., 61* (1998) 231

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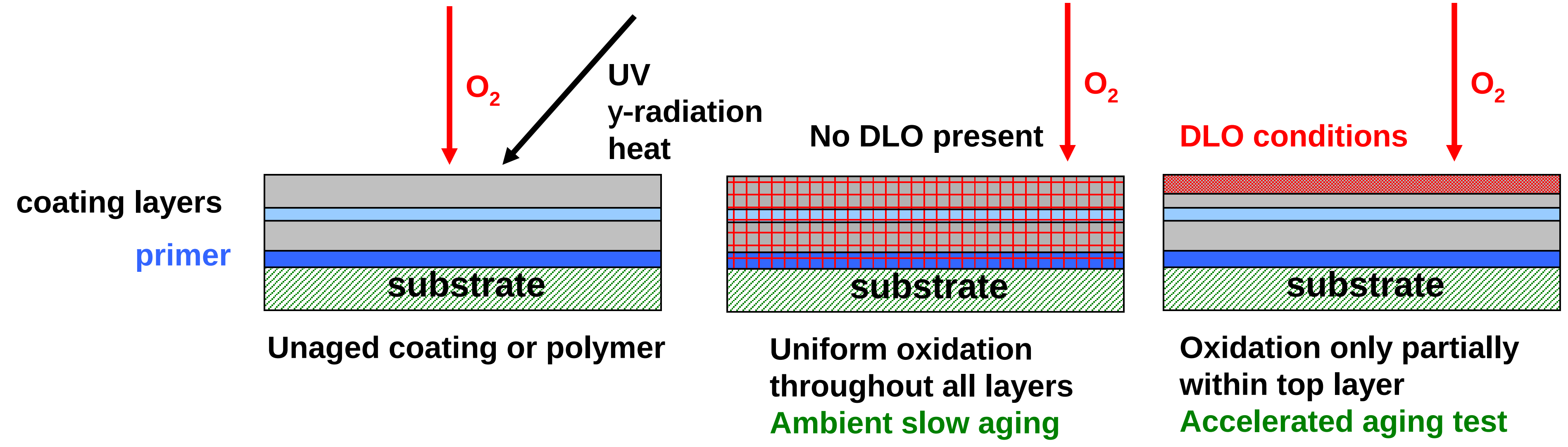
Example 1: Accelerated aging anomaly with T

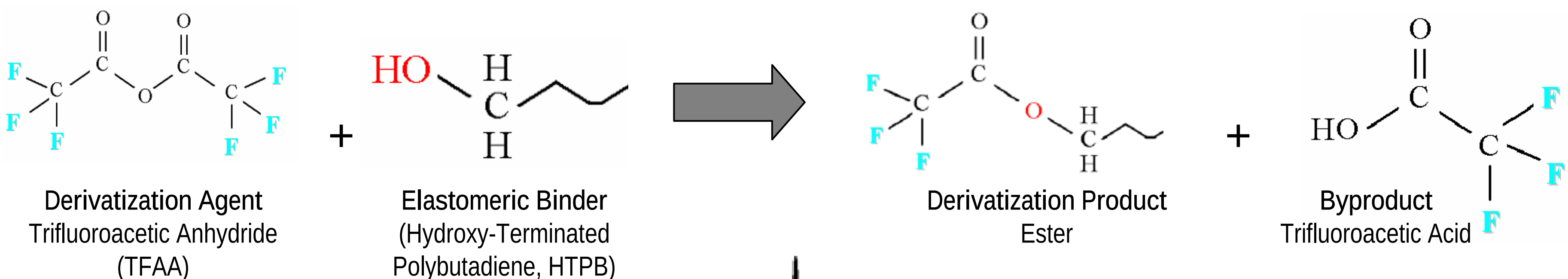
- DLO: Diffusion Limited Oxidation at elevated T
- Oxidation in material is faster than oxygen can diffuse into it
- Will lead to oxidation profile formation, heterogeneous degradation
- Oxidation rate *Φ* (consumption) versus permeability *P* (supply)
- Accelerated aging tests can completely misrepresent real aging

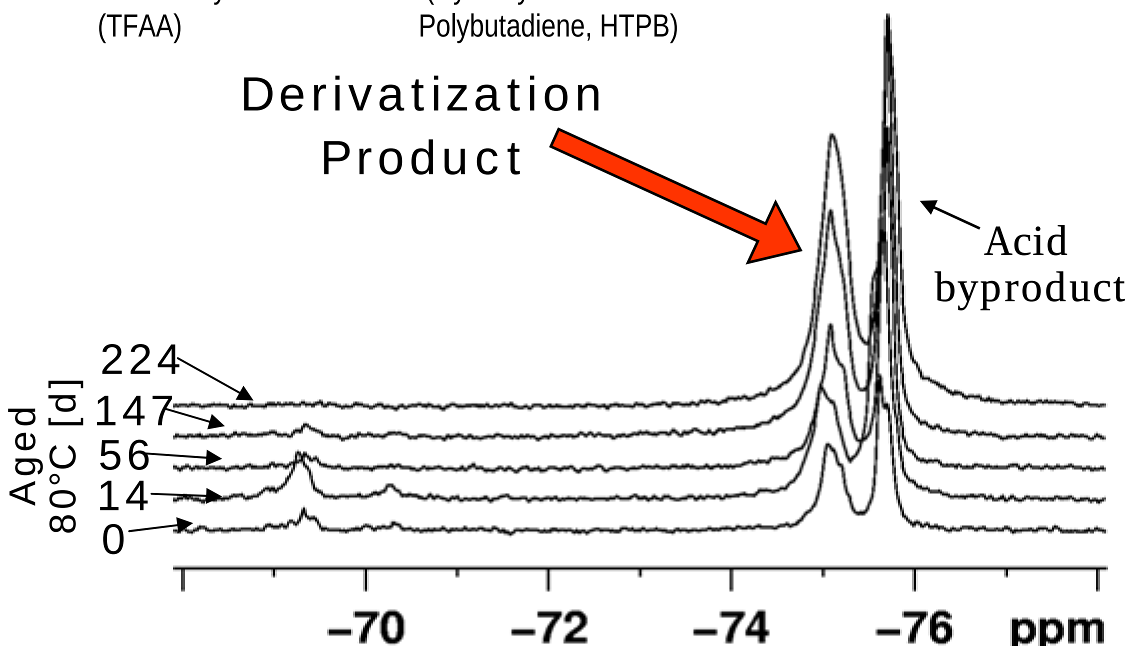


Measure or estimate *Φ* and *P* prior to conducting any accelerated aging tests!

Probing degradation with ^{19}F markers leading to enhanced NMR sensitivity

Alcohol functionalities are good indicators of oxidation
Use ^{19}F NMR to analyze derivatization product
Correlate intensity of NMR signal with extent of oxidation of polymer





- **Concentration of derivatization agent increases with degradation level**
- **Functionalities are good indicators of oxidation**

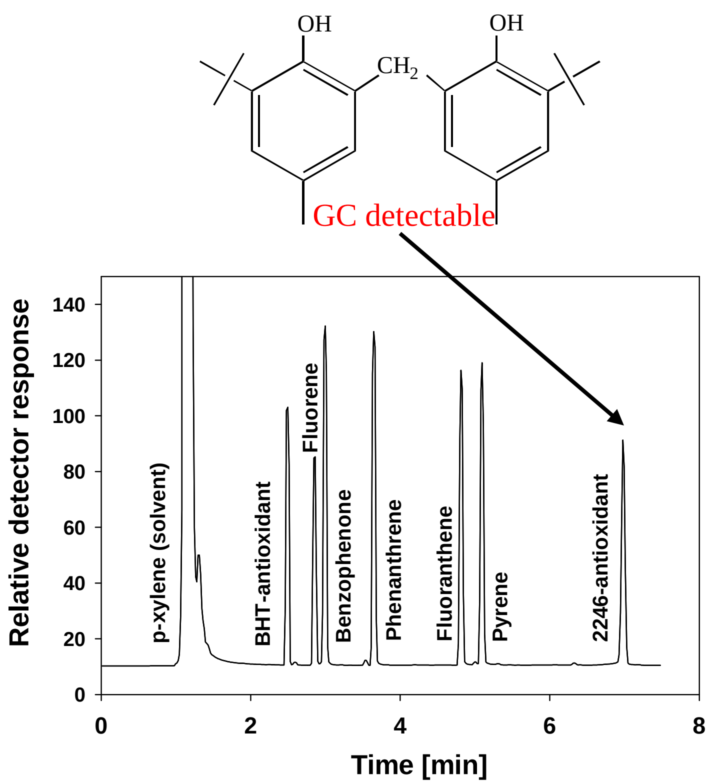
Roger Assink, Dept. 1811

J.M.Skutnik, R.A.Assink, M.Celina, *Polymer, 45* (2004) 7463

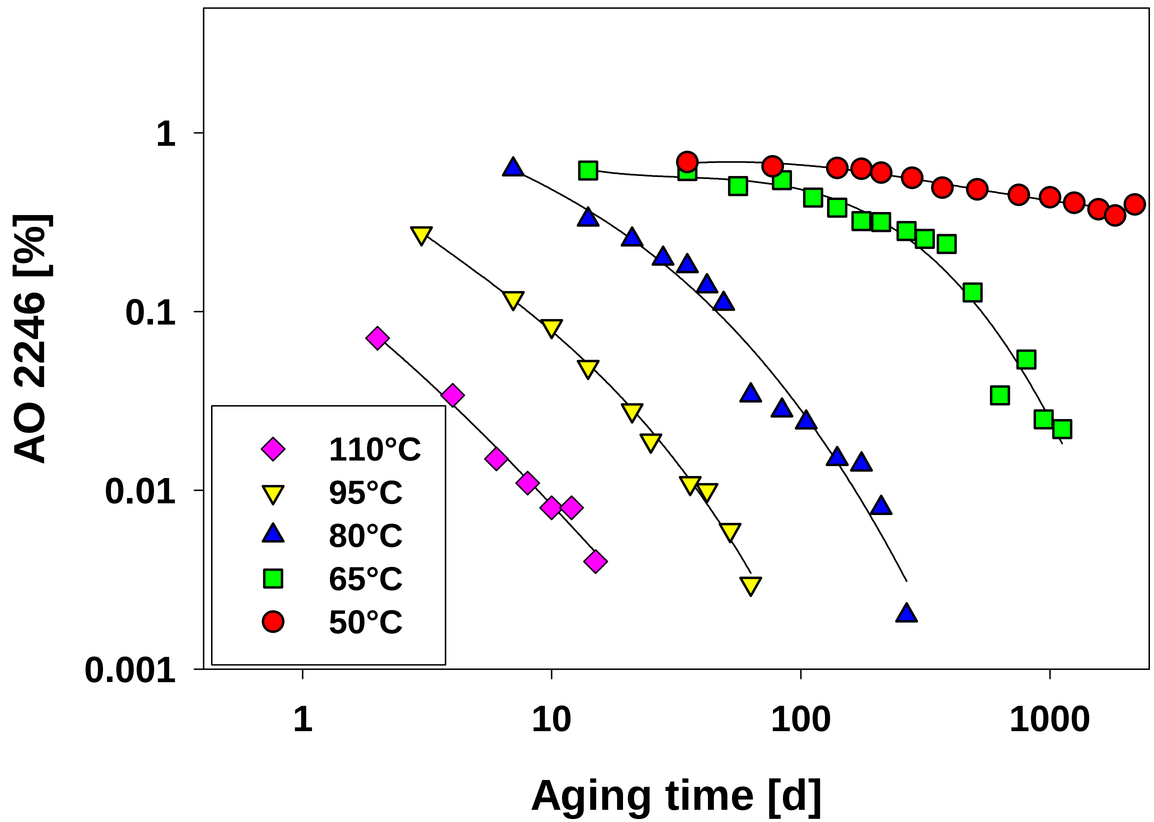
Predictive aging study of elastomer

- **Aim: Establish features of AO depletion**
- **Developed GC method**
- **Aim: Correlation of AO level with mechanical state**

Binder has 1% AO stabilizer hindered phenol 2246



Reduction in free AO with aging time



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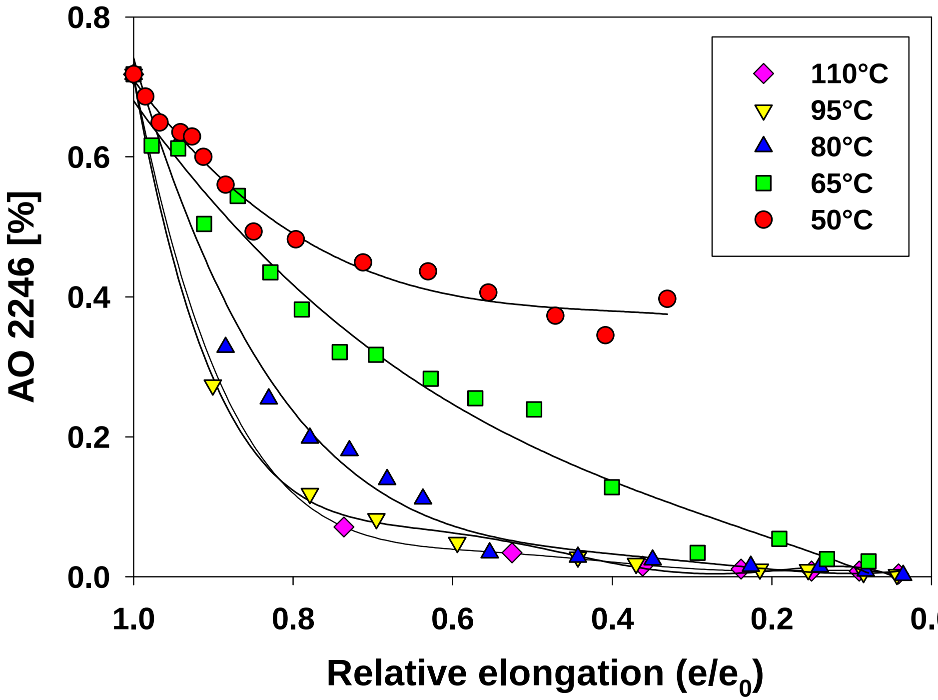
M. Celina, J. Skutnik Elliott, S. Winters, R. Assink, and L. Minier, *Poly. Deg. Stab.*, *91* (2006) 1870

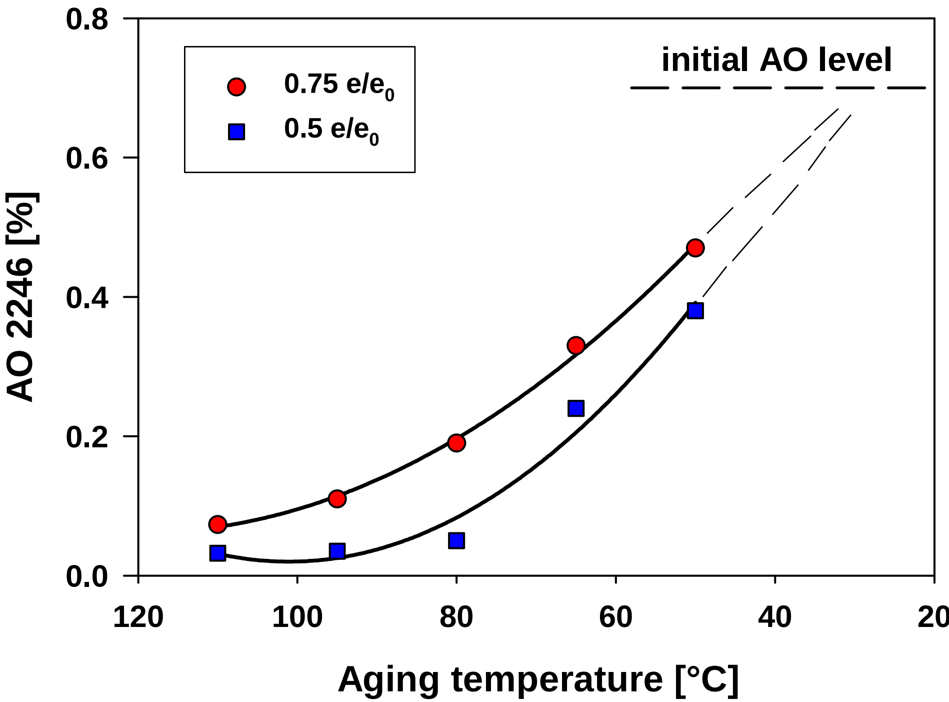
Predictive aging study of elastomer

- Rapid decrease in AO at elevated T
- Continued presence of AO at lower T

AO depletion features depends on T



Loss of mech. properties at diff. AO levels



- No universal correlation between AO level and mechanical properties
- Aging and failure will occur at low T's despite high levels of active AO

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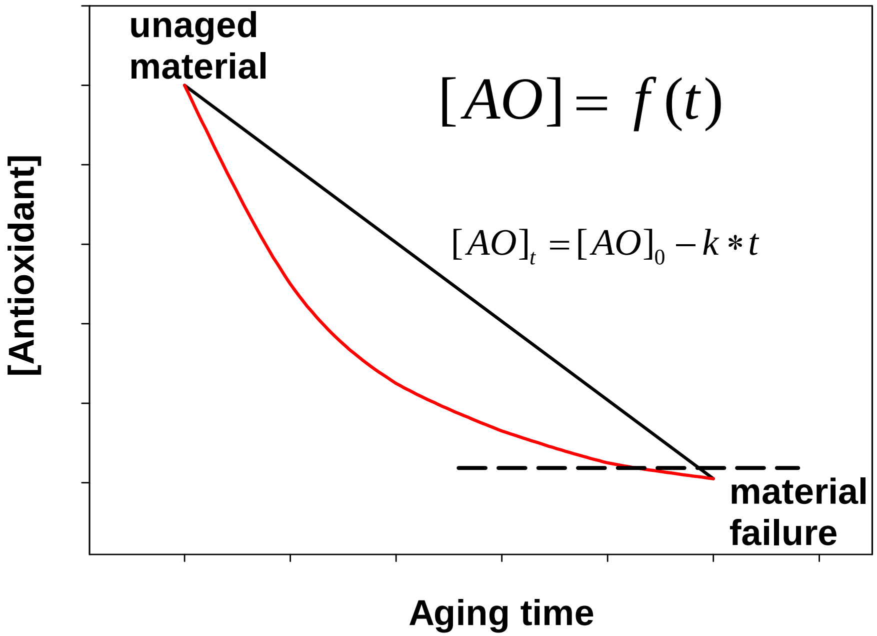
M. Celina, J. Skutnik Elliott, S. Winters, R. Assink, and L. Minier, *Poly. Deg. Stab.*, *91* (2006) 1870

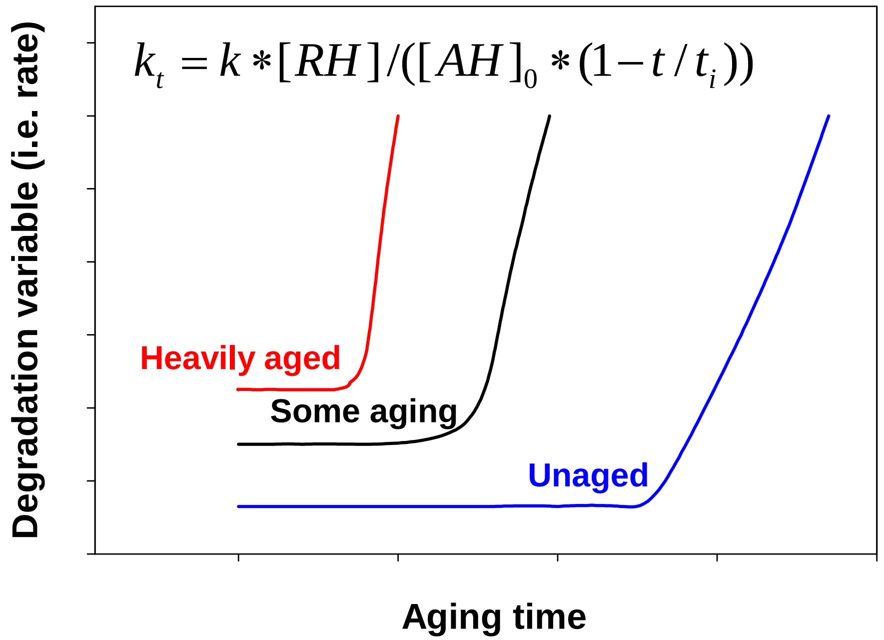
AO consumption and Wear-out behavior

- **Material failure at the end of the induction time (low AO level)**
- **How does AO consumption depend on T?**
- **Wear out concept: Prior aging leaves signature in material**
- **Accelerated aging of aged samples, determine fractional changes**

Consumption of antioxidant during aging



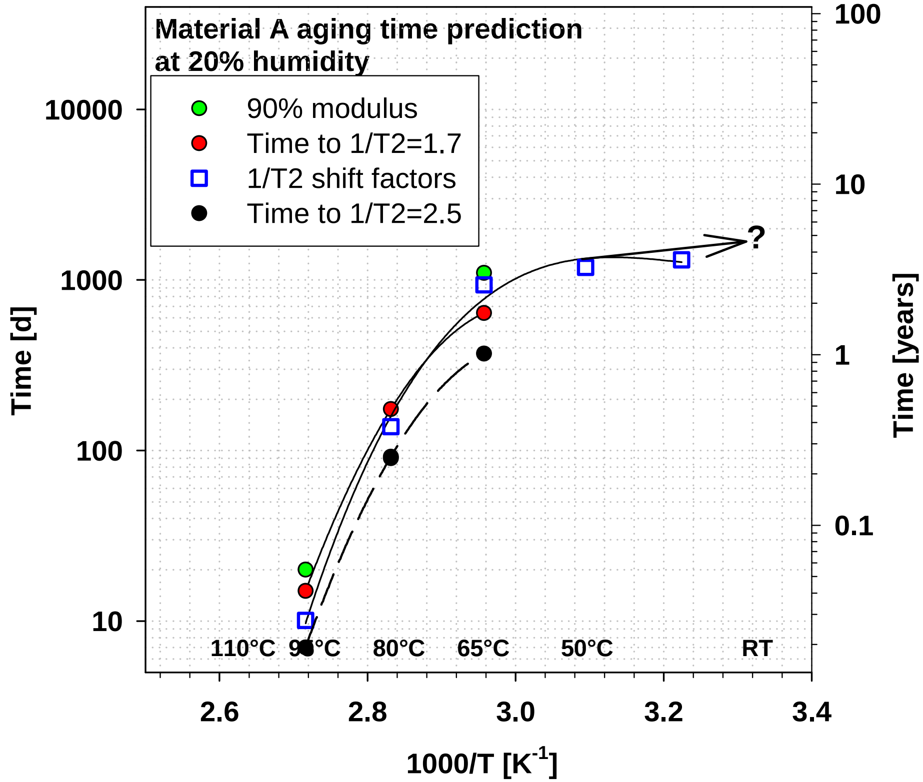
Prior aging levels affect follow-up aging

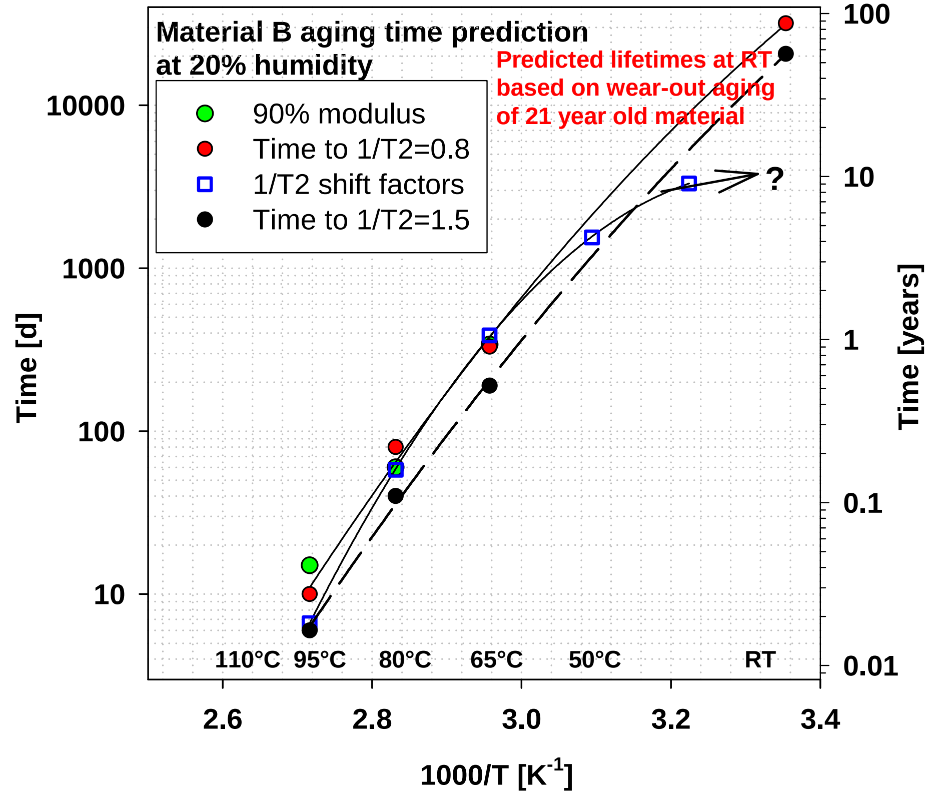


M. Celina, J. Skutnik Elliott, S. Winters, R. Assink, and L. Minier, *Poly. Deg. Stab., 91* (2006) 1870
M. Celina, A. B. Trujillo, K. T. Gillen, L. Minier, *Poly. Deg. Stab., 91* (2006) 2365

Example: Combined hydrolytic and thermal aging

- Polyurethane elastomer, lifetime estimation needed for re-qualification
- Property changes monitored via mechanical and T_2 NMR changes
- Unexpected rapid degradation at low temperatures
- Significant curvature, overestimation based on high T data

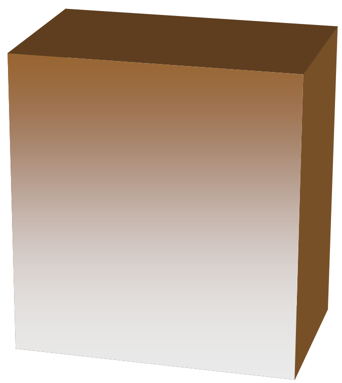




Examples of infectious processes

Ethylene gas ripens fruit

Unripe avocado + ripening apple

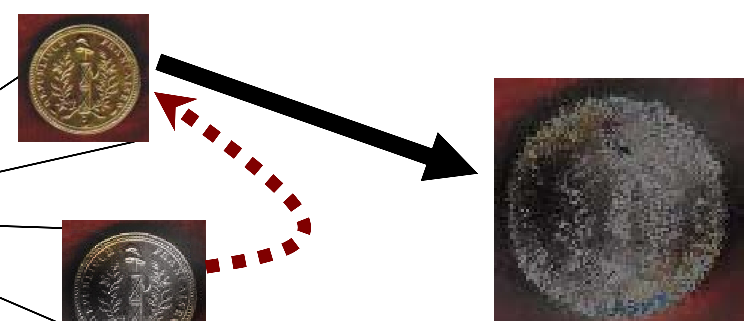


Ripening fruit releases ethylene, which causes OTHER fruit to ripen

$CH_2{=}CH_2$

ripe avocado

Tin disease causes infected metal to contaminate other metal



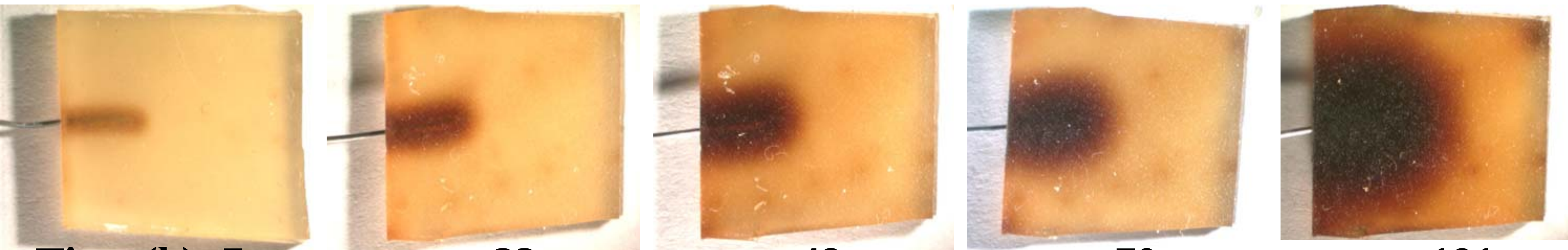
buttons degraded

Napoleon's army left Russia with their pants down

Oxidation spreading – heterogeneity – metal catalysis

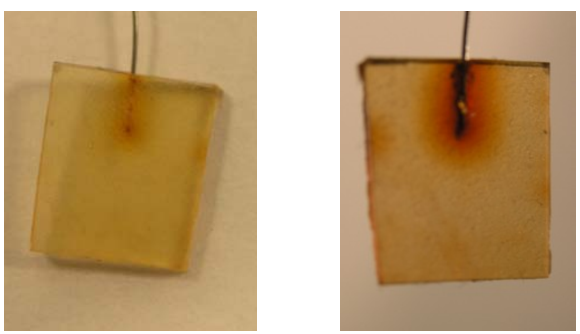
- **Tinned copper wire, copper is a well-known catalyst**
- **Example of localized degradation**

BPAN 95ºC



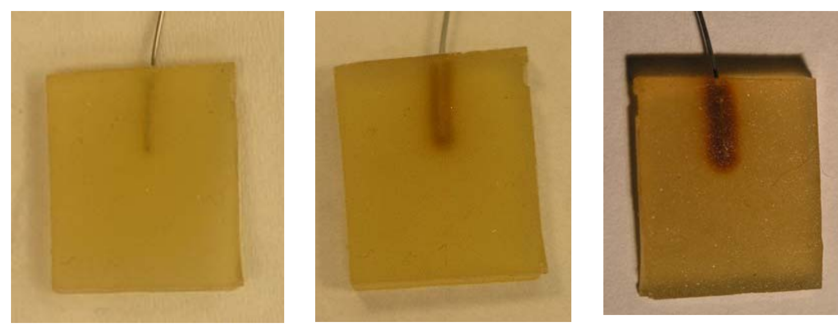
Time (h): 7 23 48 70 191

HTPB 50°C



2180h 11600h

PBAN RT



670h 3600h 12400h

We will all age rapidly while we tackle the science of aging

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A few conclusions

Lifetime predictions and performance assessments are challenging:
- Surface versus bulk conditions during accelerated aging
- Mechanistic variations with varying exposure conditions
- Heterogeneity aspects and physical dtrsibution of material changes

New techniques are available:
- Beam techniques, scanning microcopy, high resolution,
- but depends on what the characterization needs really are

What is the impact in terms of nano-technology:
- We need to know precisely know what we measure
- We need to know how it relates to the material properties
- Multiple techniques and combined approaches will provide increased confidence and more reliable performance predictions

• Understand your materials, aging conditions, and characterization techniques as best as possible to conduct meaningful accelerated aging tests!

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Tim Dargaville, Leanna Minier, Julie Skutnik

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