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Thermal degradation as a function of temperature and its relevance to lifetime prediction and condition monitoring

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Roy W. Tess Award Symposium on Durability and Service Life Prediction of Polymeric Materials in Honor of Jonathan Martin,
ACS San Francisco, 9/11/2006

Our challenge: To better understand the influence of temperature on long-term thermal aging of polymers

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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 – Optimization of Materials Accelerated Aging - Predicting Polymer Lifetimes

Our broader interests are:

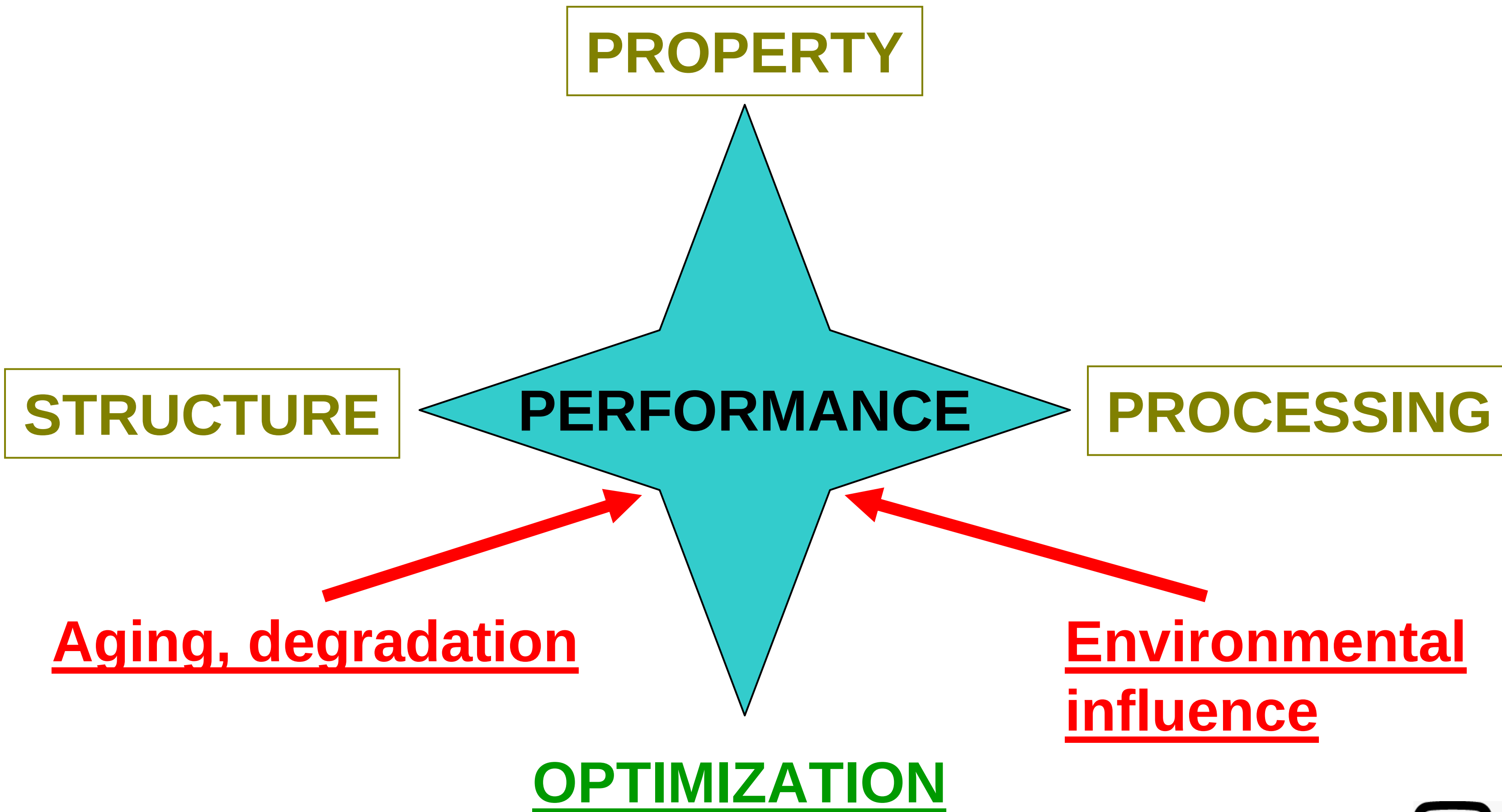
- Understanding the performance of industrial materials
- Developing methods and techniques for accelerated aging of materials
- Develop strategies for lifetime prediction methods
- Using specific materials to better understand polymer degradation
- Combine physical and chemical analyses with modeling

• Key issues and targets for this presentation:

- We need to better understand the science of accelerated aging
- Arrhenius extrapolation versus non-linear behavior with T
- Accelerated aging, how to extrapolate ?
- Are there anomalies in accelerated aging due to temperature?

High performance polymer materials

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



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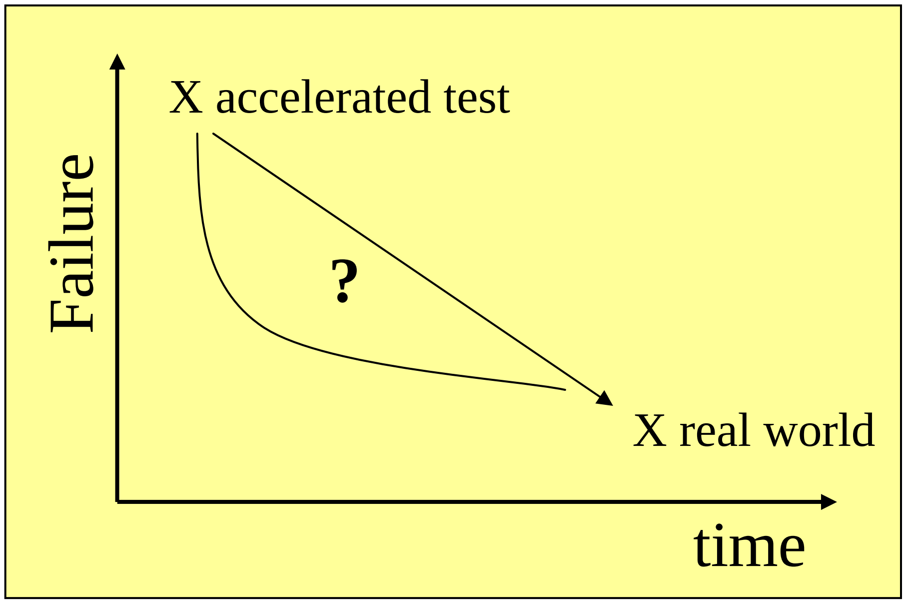
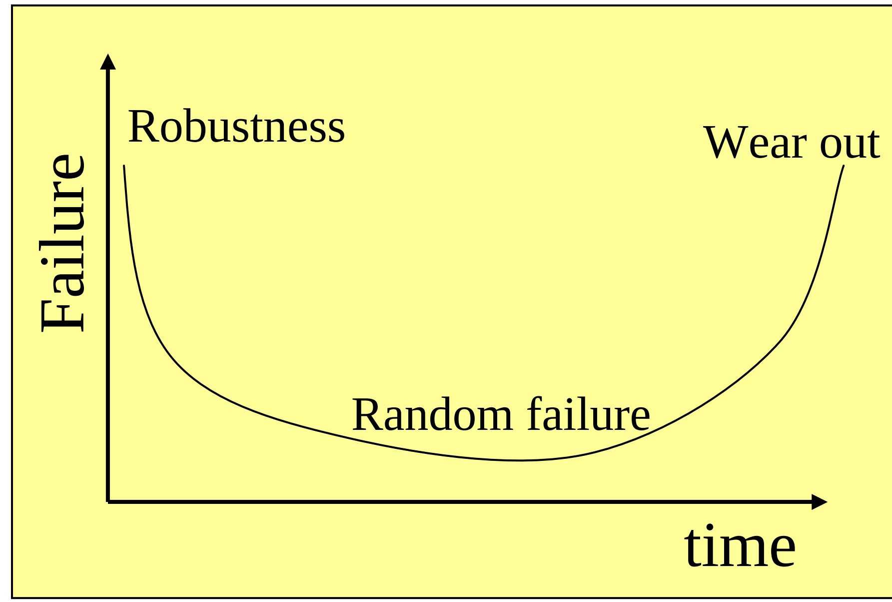
Failure processes - time dependency

- **Infant mortality controlled by material robustness**
- **Random failure**
- **Wear out, autocatalytic failure increase, final life**



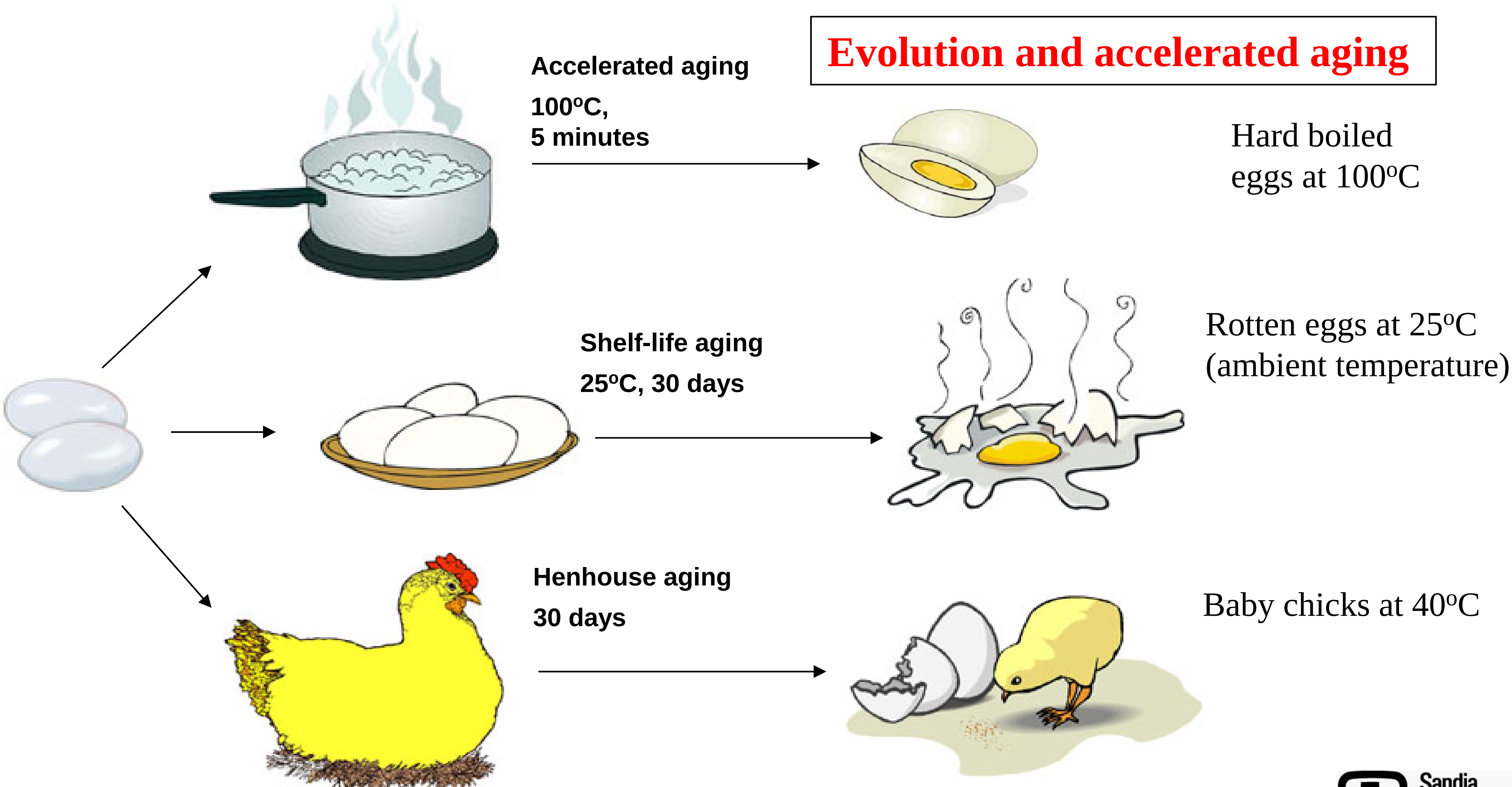


Extrapolations
Arrhenius
Inverse power law
Eyring
WLF

Failure modes to be established
Determine acceleration factors
Variability in acceleration of aging mechanism
Variability in sample to sample
Static versus dynamic aging exposure
(just oven exposure or cyclic stresses, annealing)

Reactions may change with temperature

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



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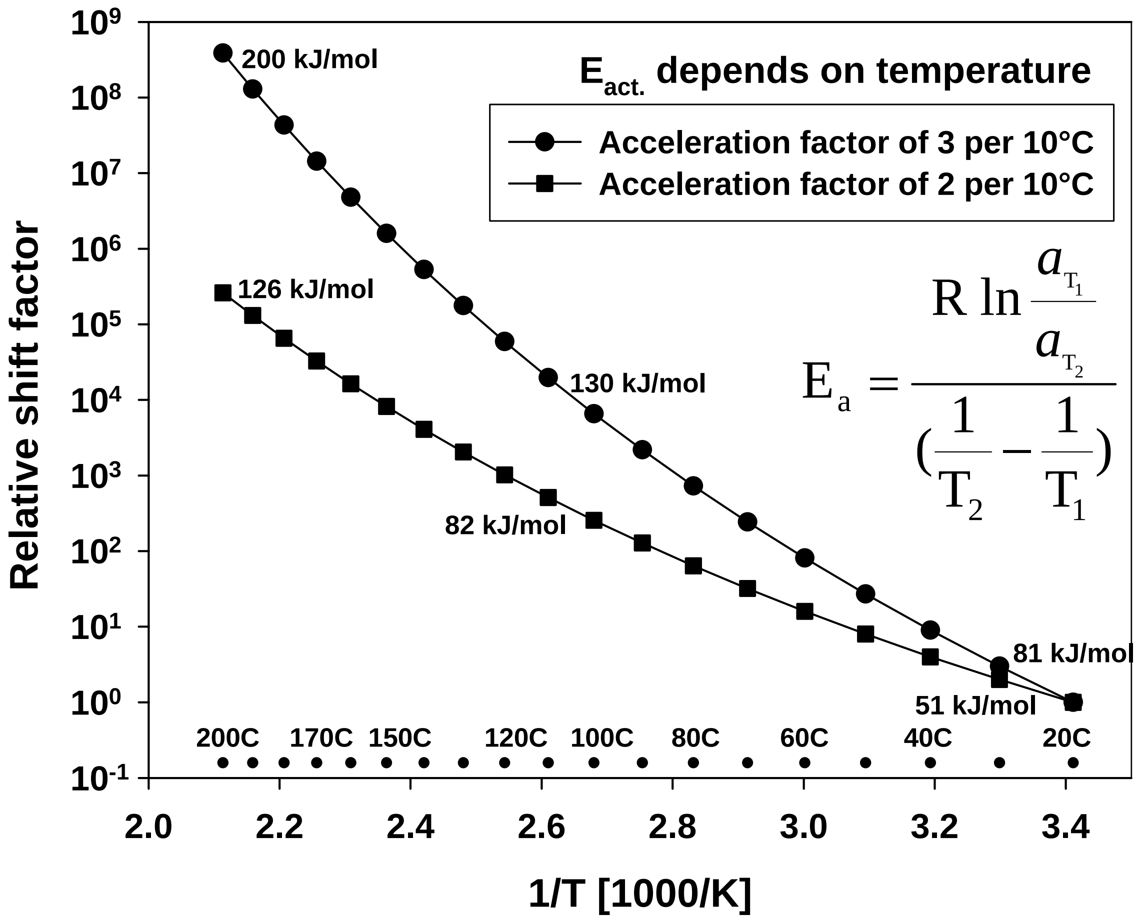
Accelerated aging - 2 to 3 times faster per 10°C ?

- **Rule of thumb, widely used in chemistry (reaction kinetics)**
- **Increase T by 10°C, results in 2 to 3 times faster reaction**
- **Approach implies that Ea. will depend on T**
- **Will result in curvature for Arrhenius plot**

Constant shift factors imply Ea will depend on T

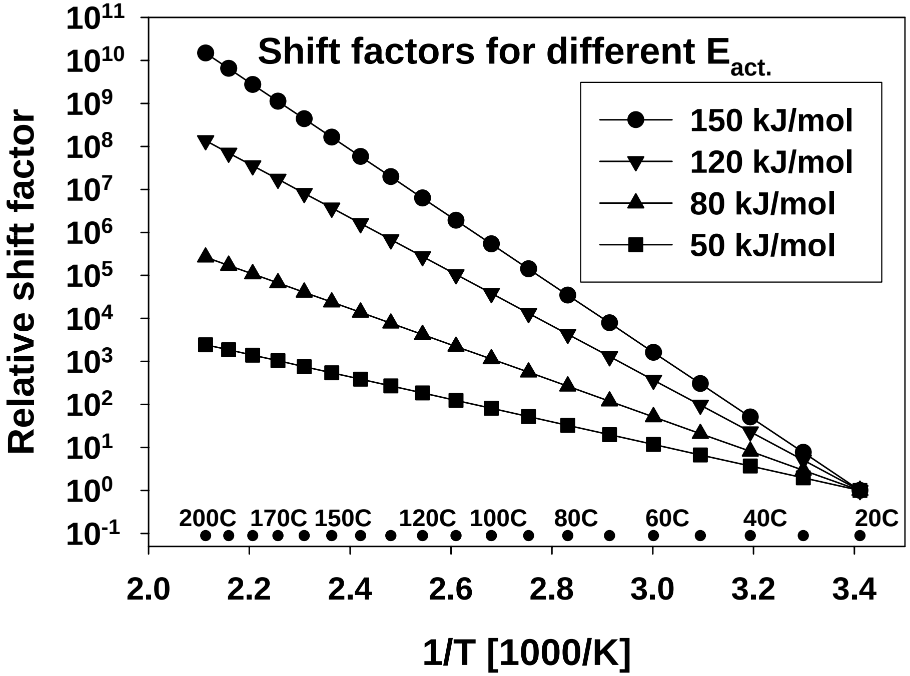
Conflicts with Arrhenius methodology

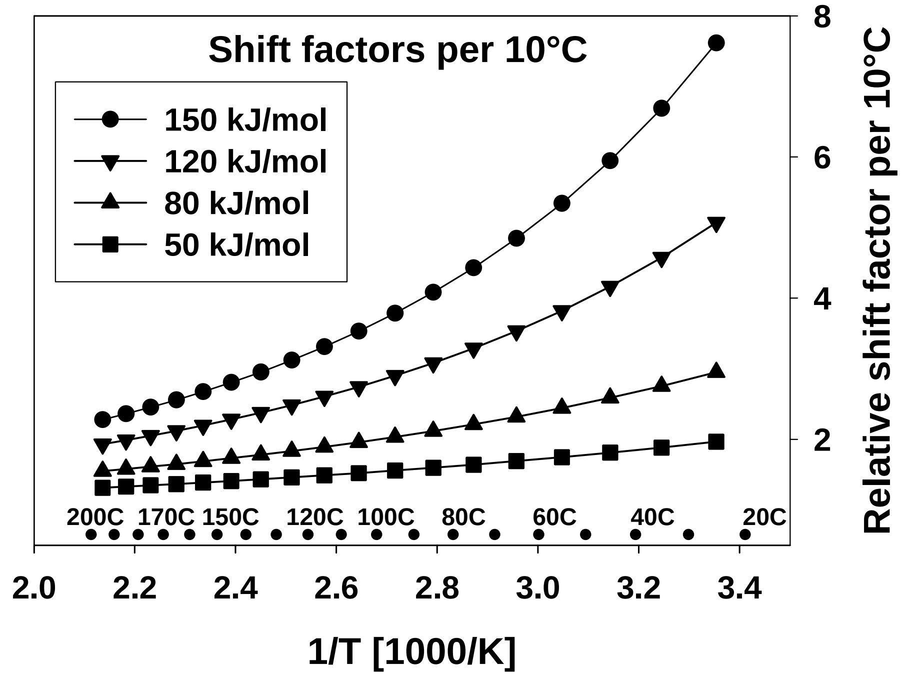


$$E_a = \frac{R \ln \frac{a_{T_1}}{a_{T_2}}}{\left(\frac{1}{T_2} - \frac{1}{T_1}\right)}$$

Accelerated aging of materials - constant Eact.?

- **Arrhenius approach to accelerated aging**
- **Aging kinetics described by liner Arrhenius plot with constant Eact.**
- **Considerable acceleration even for moderate Eact. And T range**
- **Relative acceleration will depend on temperature range**
- **Shift factor of 10^6 equal to 1d vs. 2740 years**

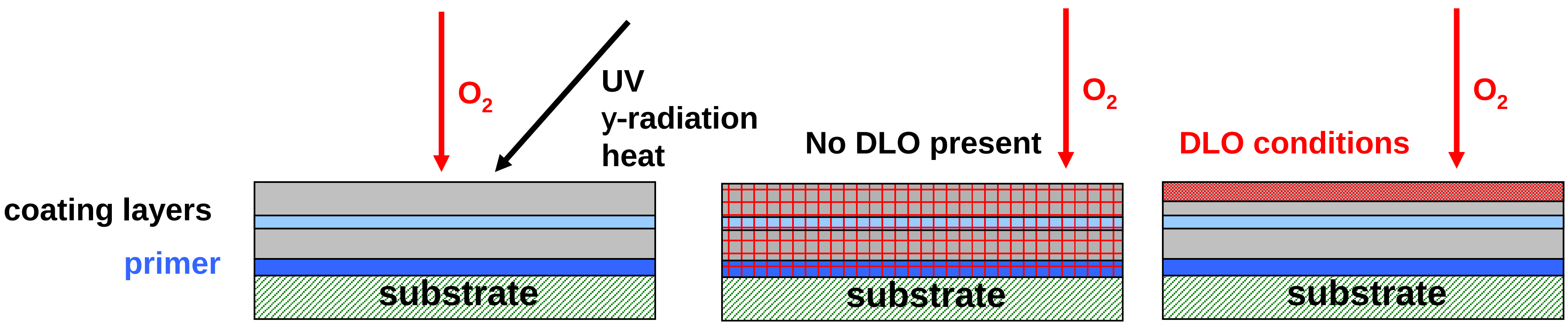




Constant E_{act} implies relative acceleration will depend on T

Example 1: Accelerated aging anomaly with T

- **DLO: Diffusion Limited Oxidation**
- **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**



Unaged coating or polymer

Uniform oxidation throughout all layers
Ambient slow aging

Oxidation only partially within top layer
Accelerated aging test

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

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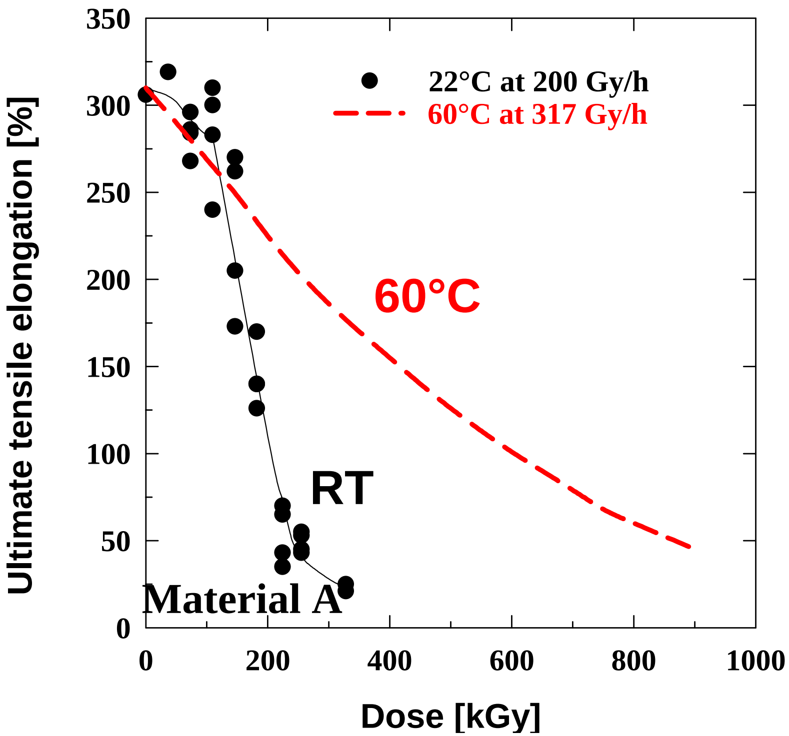
Example 2: Mechanistic anomaly with T

- **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**
- **Relevant to photo-oxidation?**

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

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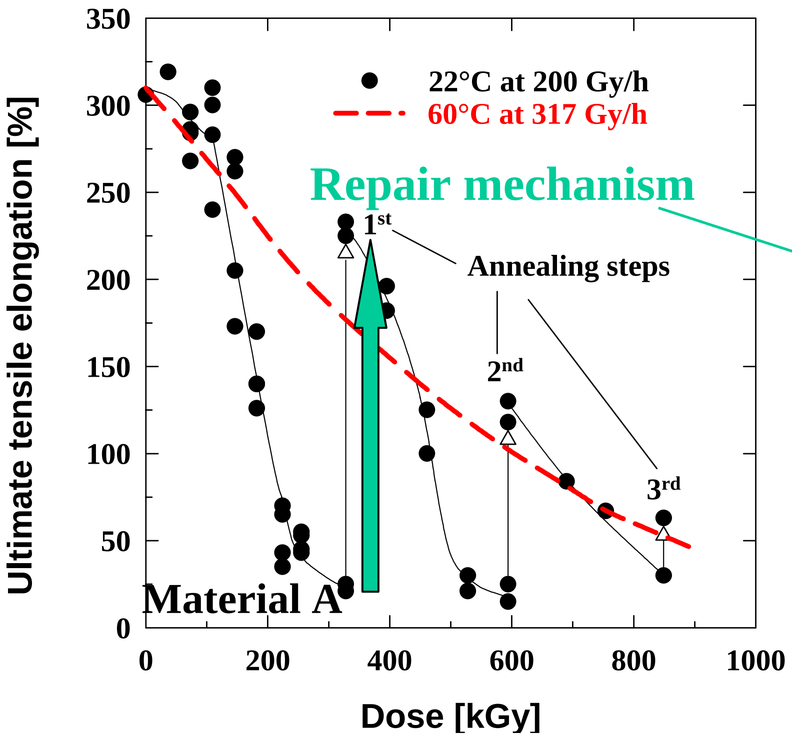
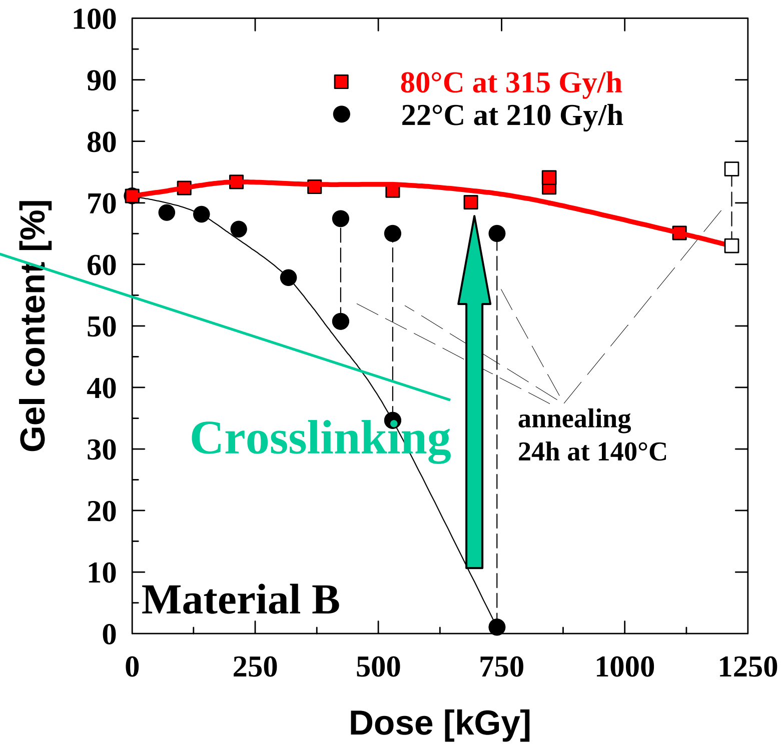
Example 2: Mechanistic anomaly with T

- 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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Polymer Performance – Optimization of Materials Accelerated Aging - Predicting Polymer Lifetimes

Some examples of our approaches:

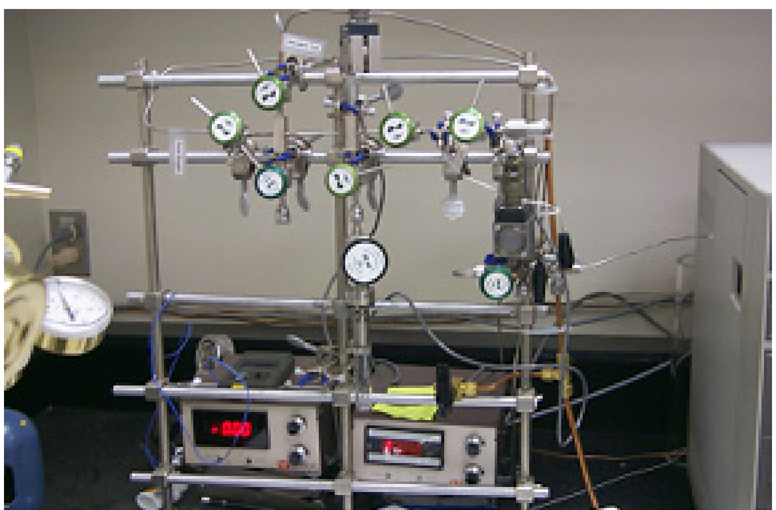
- **Oxygen consumption, oxidation rate measurements over large temperature range**
- **Analysis of AO consumption with aging**
- **Chemiluminescence for condition monitoring**

Required for meaningful aging study:

- **Need to have large set of samples**
- **Need long-term aging experiments over large T range**
- **Time = $$$ = aging !**

Oxygen consumption-Predicting aging at low T's

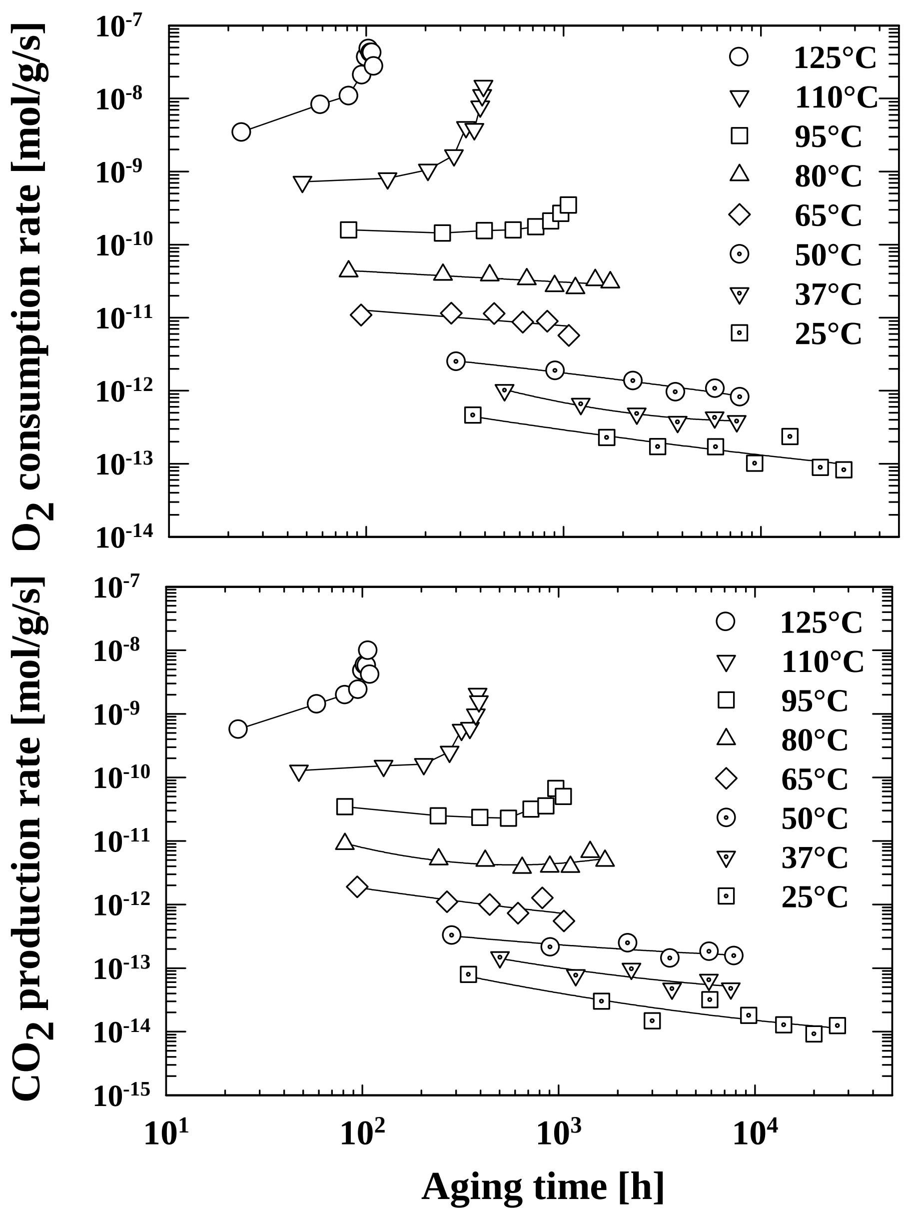
- **Manifold, ampoules, GC-analysis, P transducer**
- **Fill ampoules to P_{O2} required**
- **Determines consumed O_2 and produced CO_2/CO**
- **High dynamic sensitivity, polymer/free gas volume**
- **Measures oxidation rates ranging from 10^{-8} to 10^{-13} mol/g-s**
- **Experiments require days to 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**



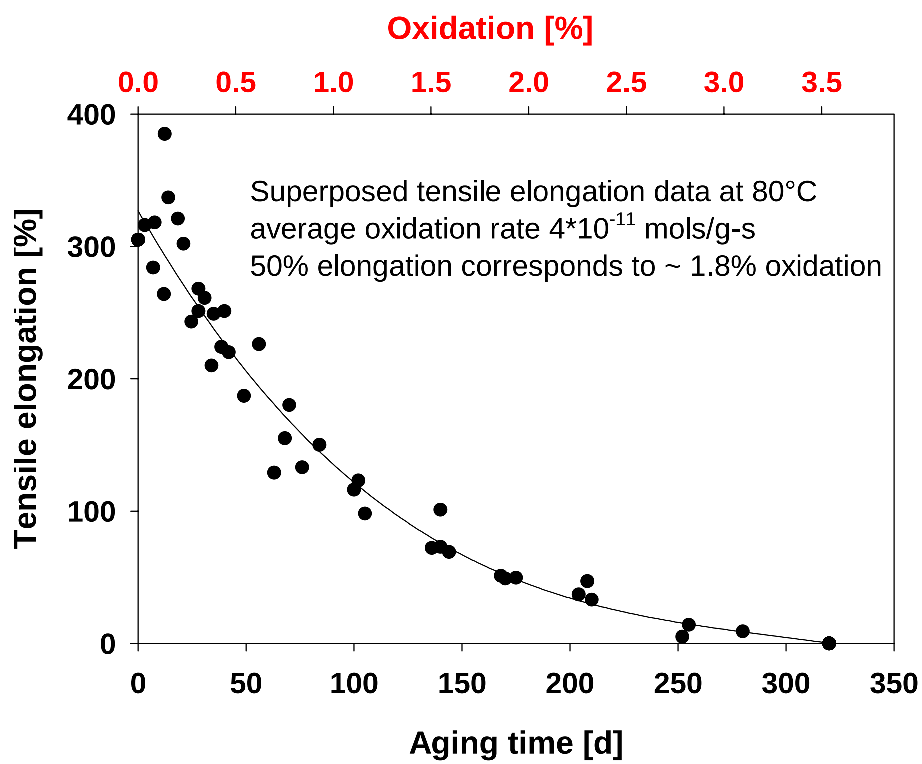
Note: Rates are corrected for increase of P with T, dissolved gas and volatiles

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



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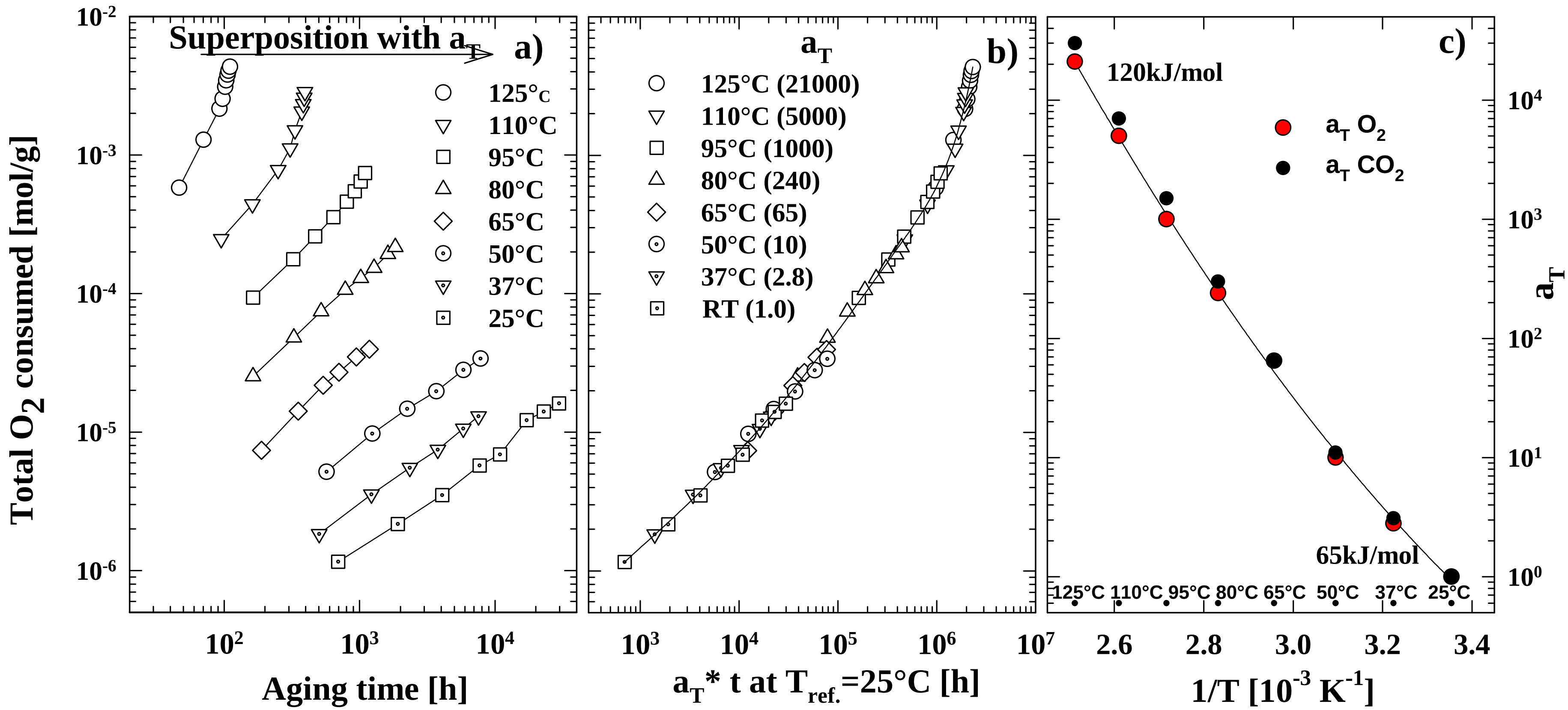
Oxygen consumption-Predicting aging at low T's

- 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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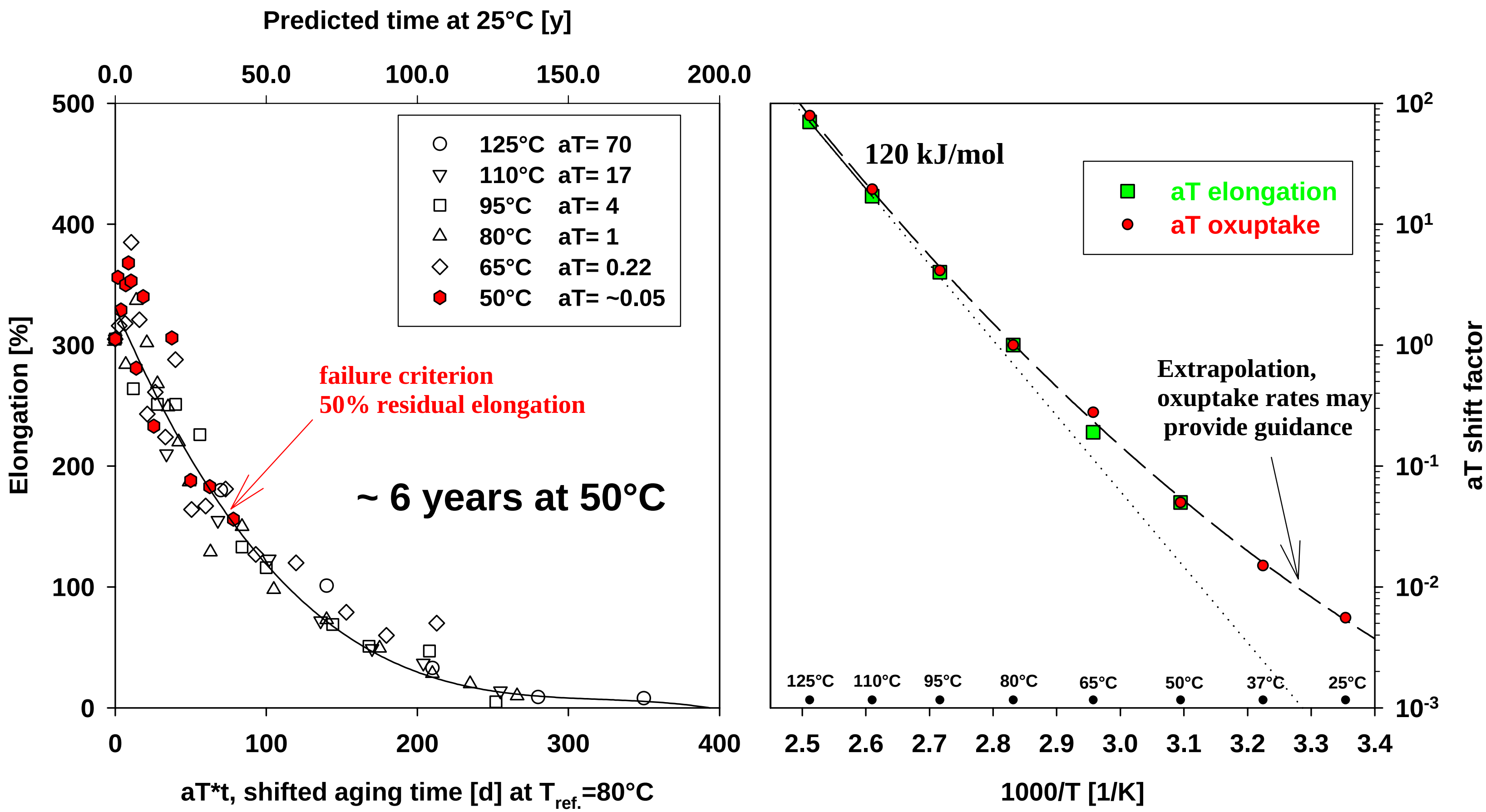
Oxygen consumption correlates with mechanical property changes

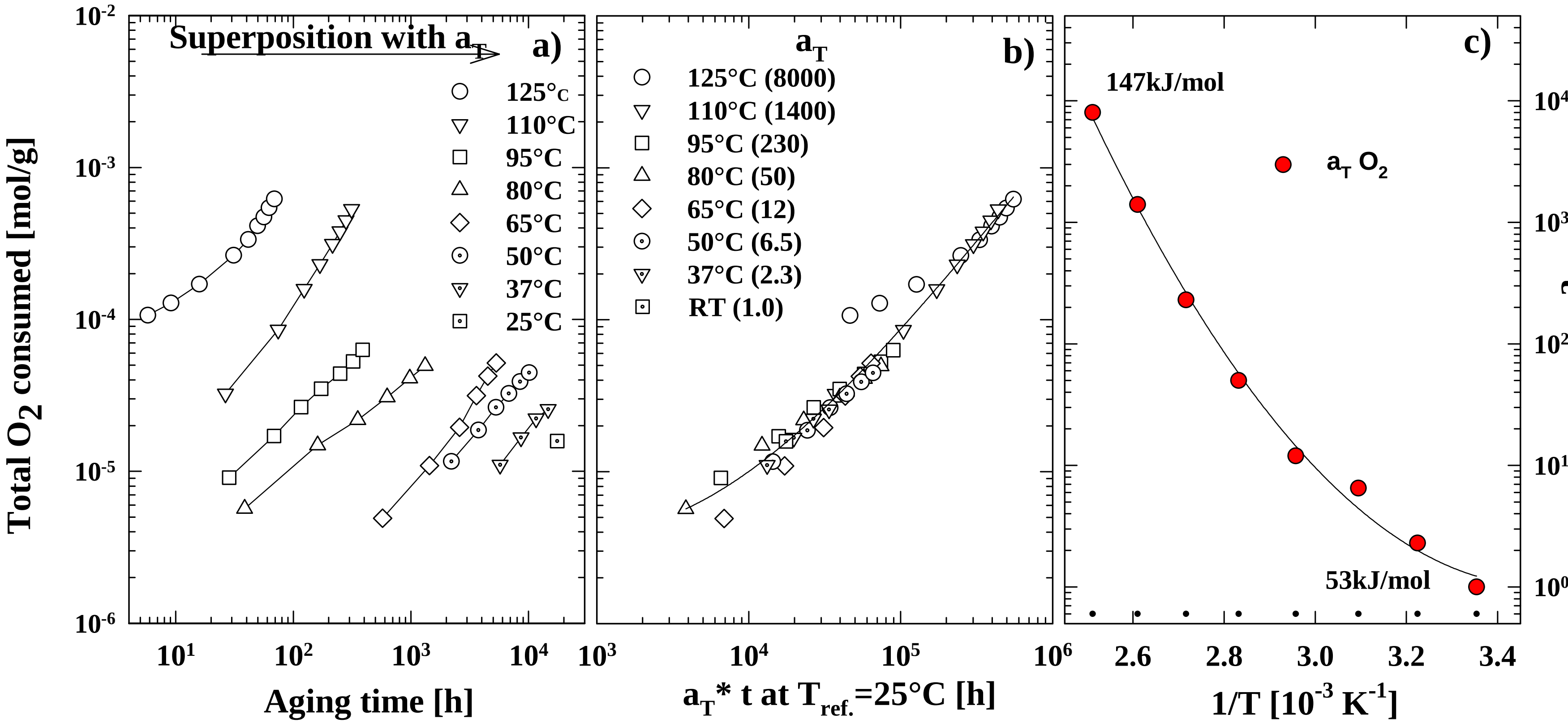
- Oxygen consumption yields data over large T range
- Non linear extrapolation, change to lower $E_{act.}$ with T
- Oxuptake predicts mechanical properties down to ambient



M. Celina, A. Graham, K. Gillen, R. Assink, and L. Minier, *Rub. Chem. Tech. 73* (2000) 680

Oxygen consumption- Pure antioxidant powder

- First time: Analysis of pure phenolic antioxidant (2246)
- Strong dependence of oxidation rates on temperature
- Similar Arrhenius curvature as in the stabilized elastomer



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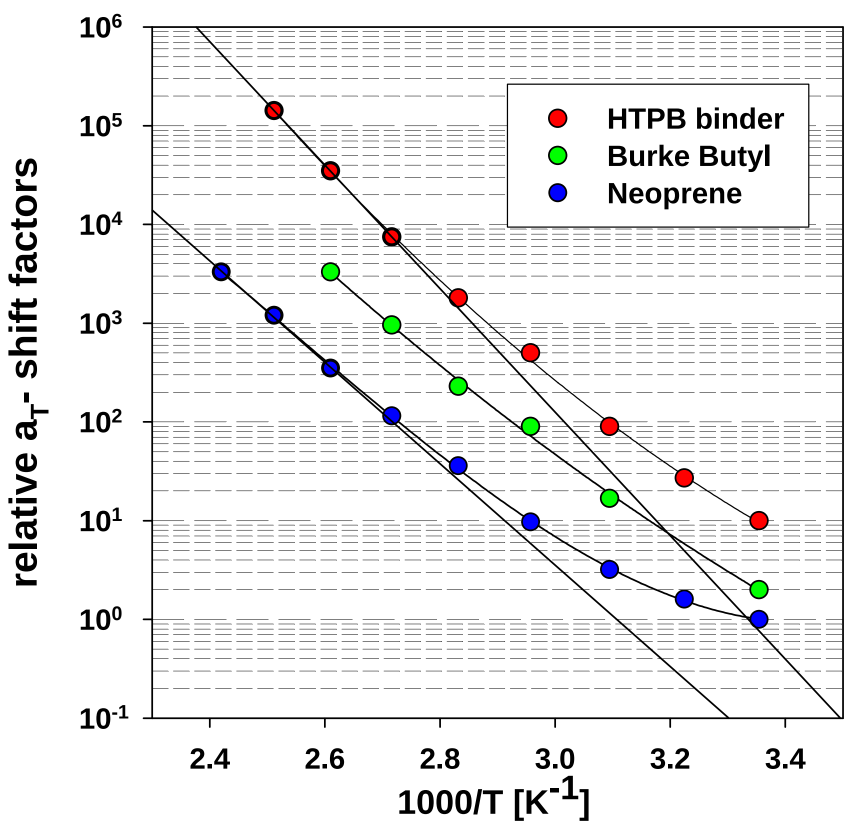
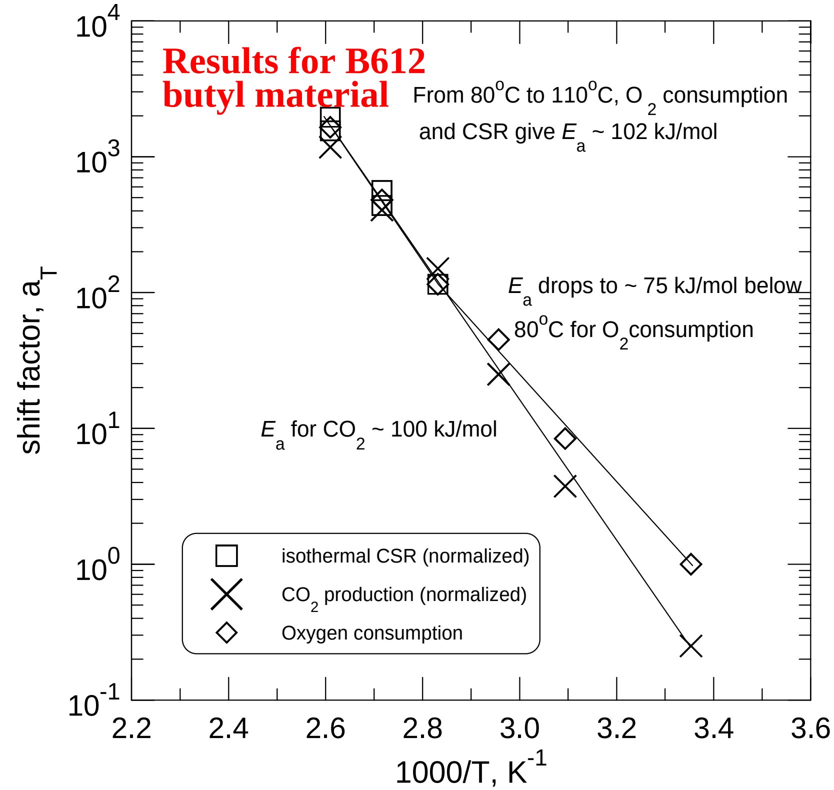
Is there a chemical reason for Arrhenius curvature?

- **Explored mechanistic variations between high and low T aging**
- **Curvature in Arrhenius plots observed for many materials**
- **Evidence for mechanistic changes, i.e. more CO_2 production at high T's**





K. Gillen, M. Celina, R. Clough, J. Wise, *Trends in Polymer Science, 5* (1997) 250
M. Celina, A. Graham, K. Gillen, R. Assink, and L. Minier, *Rub. Chem. Tech. 73* (2000) 680
K. Gillen, R. Bernstein, D. Derzon, *Poly. Deg. Stab., 87* (2005) 57

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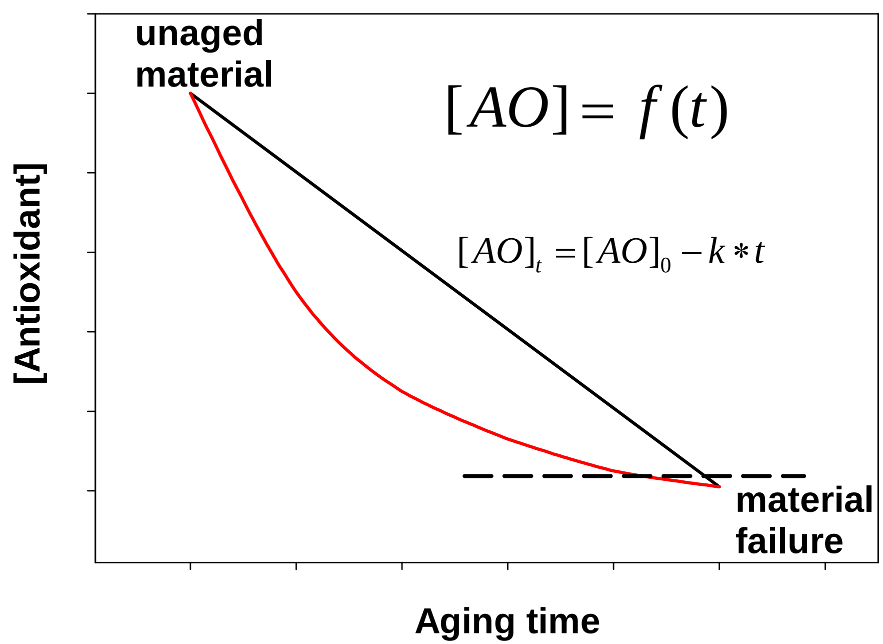
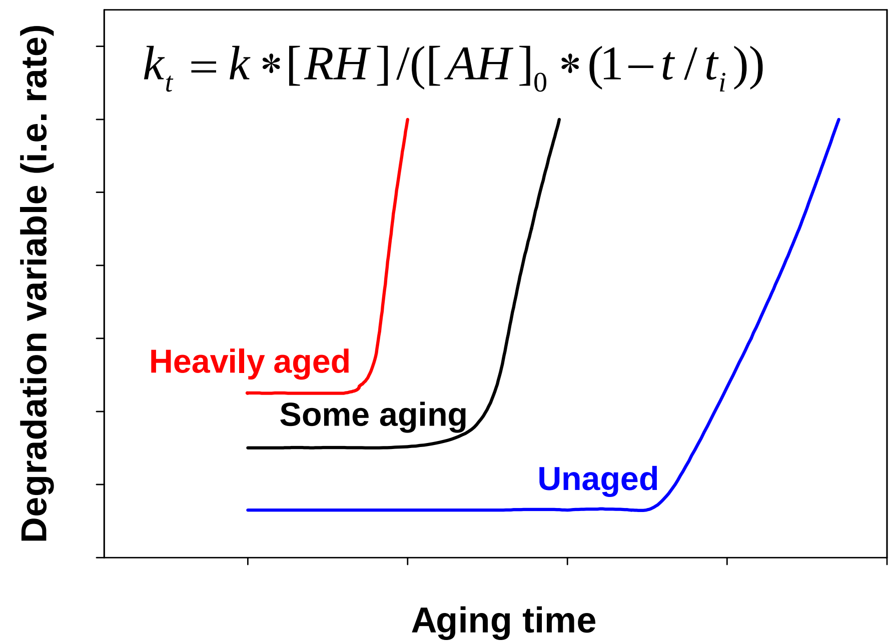
AO consumption and Wear-out behavior

- **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

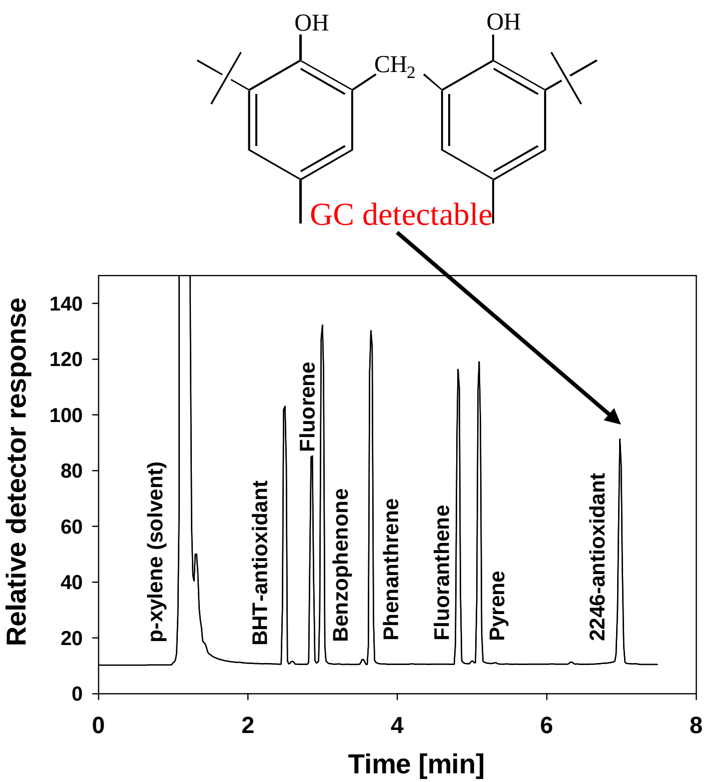


M. Celina, J. Skutnik Elliott, S. Winters, R. Assink, and L. Minier, *Poly. Deg. Stab.*, *91* (2006) 1870
M. Celina, A. B. Trujillo, K. T. Gillen, L. Minier, *Poly. Deg. Stab.*, *91* (2006) 2365

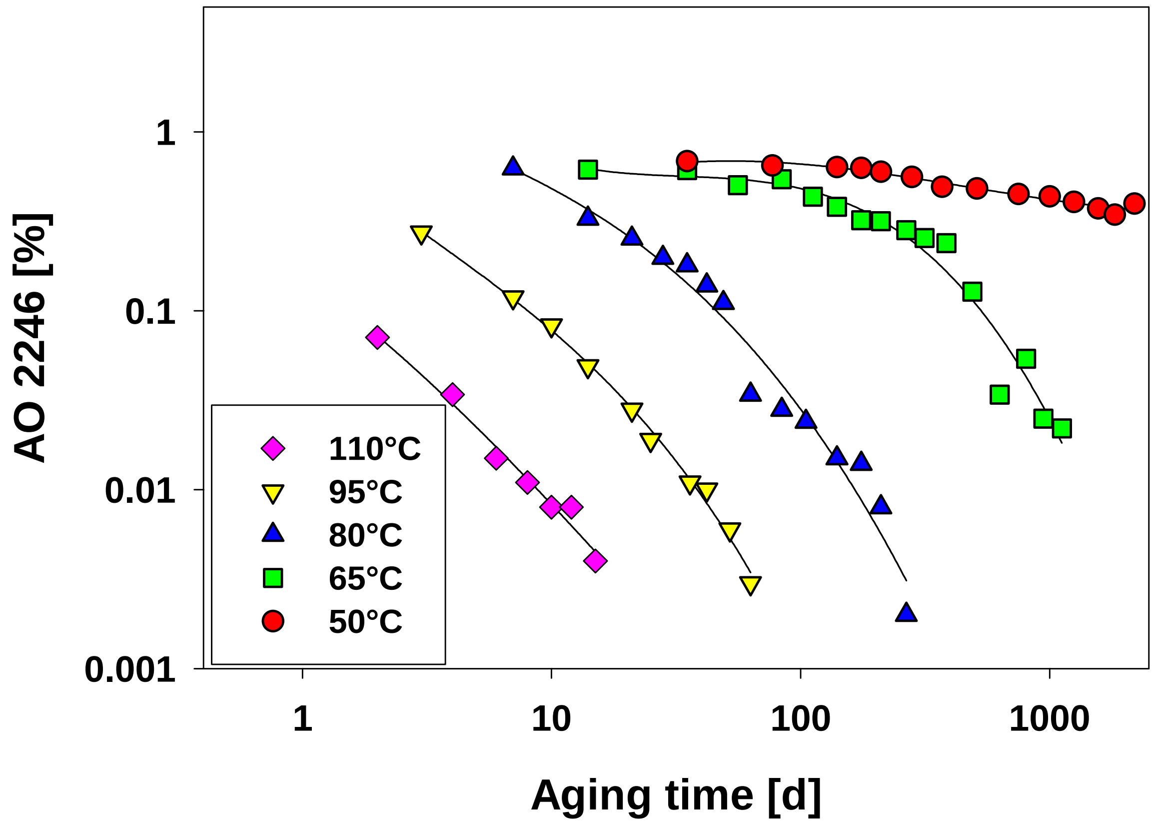
Predictive aging study of elastomer

- **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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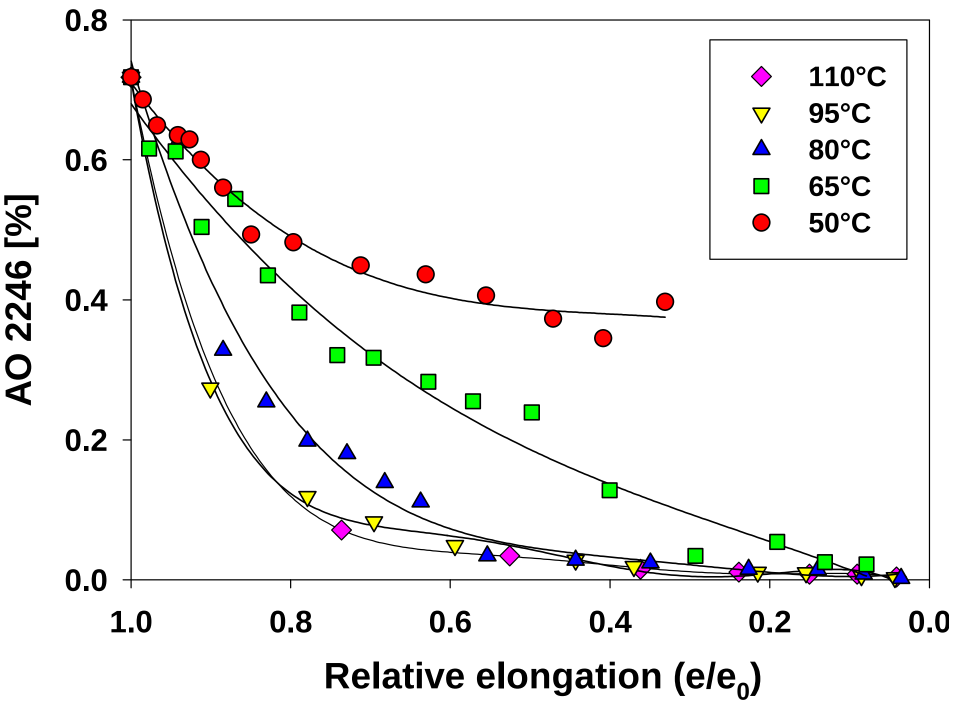
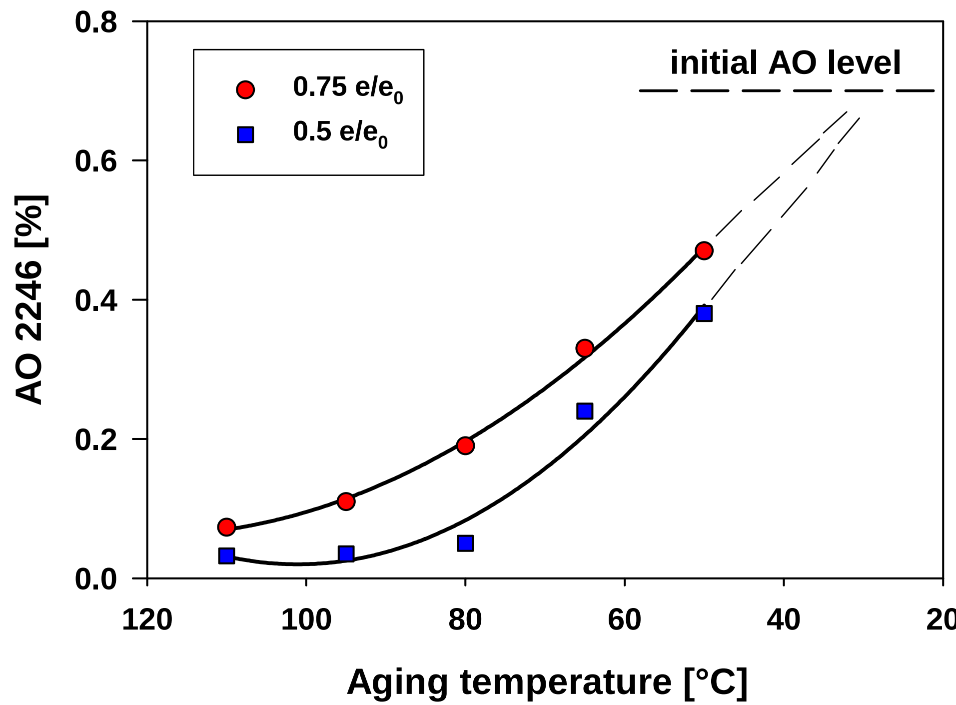
Predictive aging study of elastomer

- 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

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

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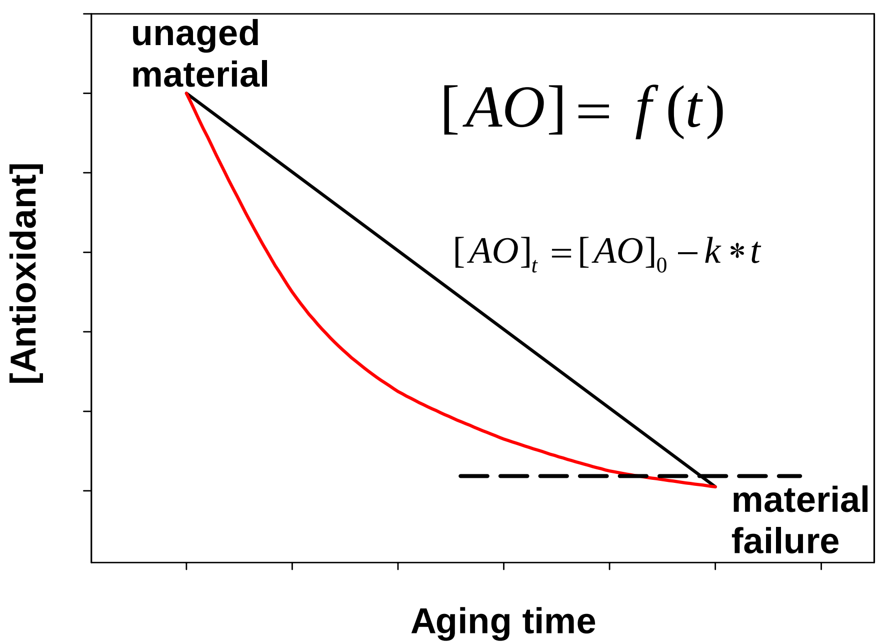
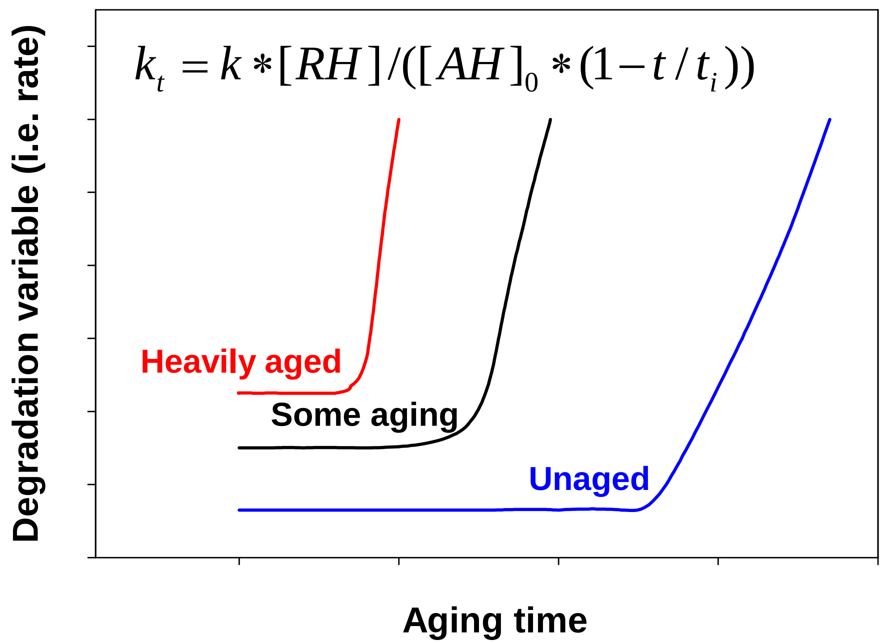


Prior aging levels affect follow-up aging



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M. Celina, A. B. Trujillo, K. T. Gillen, L. Minier, *Poly. Deg. Stab., 91* (2006) 2365

Chemiluminescence (CL) in Polymer Degradation

- CL accompanies oxidative aging processes
- Weak photon emission in the visible
- Provides feedback on degradation processes
- Photon counting apparatus required
- Sensitive technique for fundamental studies
- In-situ studies and analysis of aged materials

sensitive photomultiplier detection

Aims:
- Use CL as a condition monitoring technique
- Isothermal 'Wear-out' aging via in-situ CL

+ CL photon

aging
T, O_2

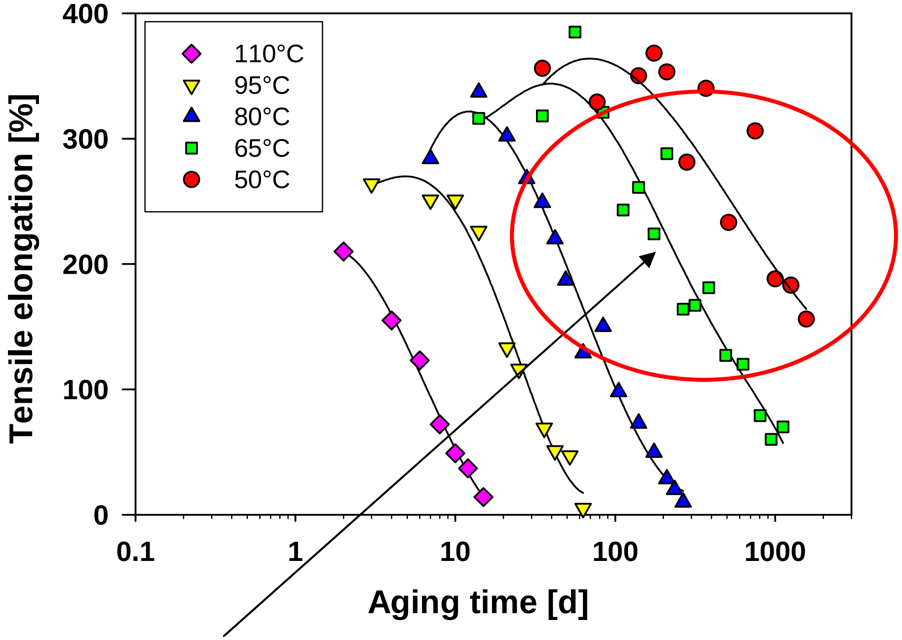
aged polymer,
chain defects with
reactive species, i.e. hydroperoxides

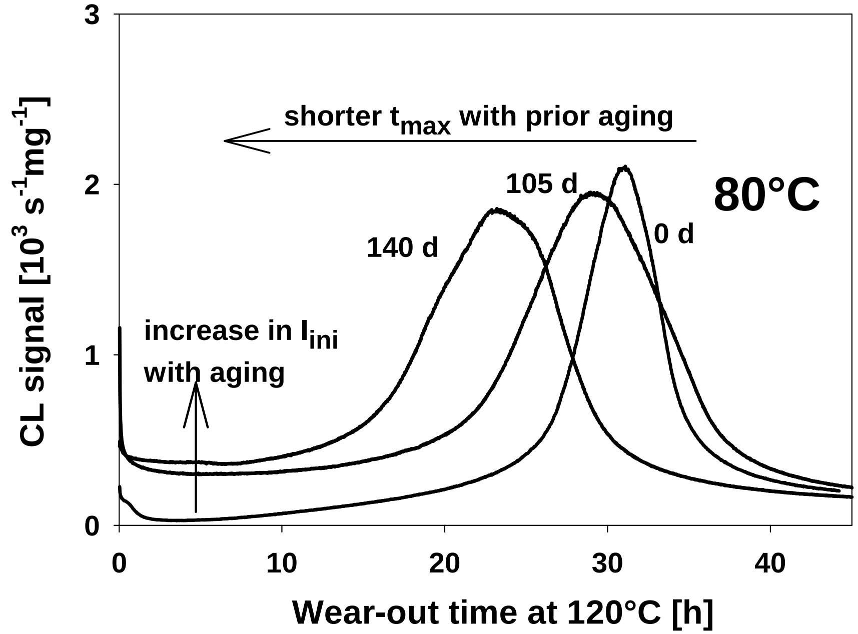
chemical condition probing

+ CL photon

CL condition monitoring of aged HTPB material

Decrease in E_t with aging time





- Use pre-aged samples and apply ‘Wear-out’ aging at elevated T

- Detect isothermal CL with time
- under O2 (i.e. at 120°C)

- Observe shorter times to maximum CL with previous aging
- Sensitive increase in initial rate with previous aging

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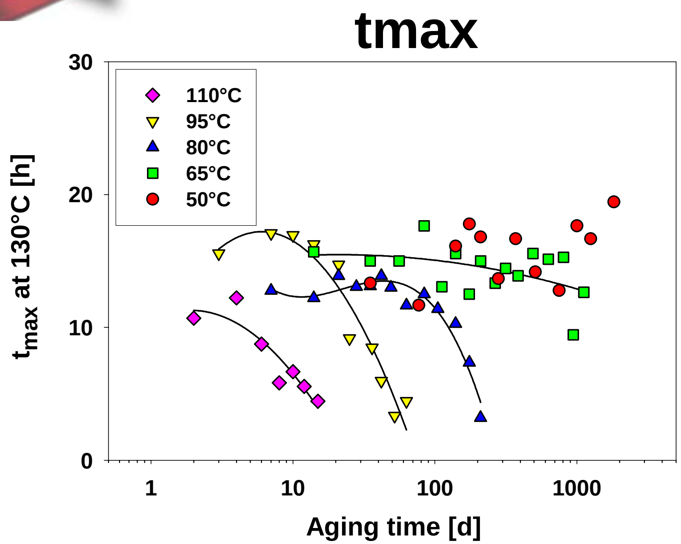
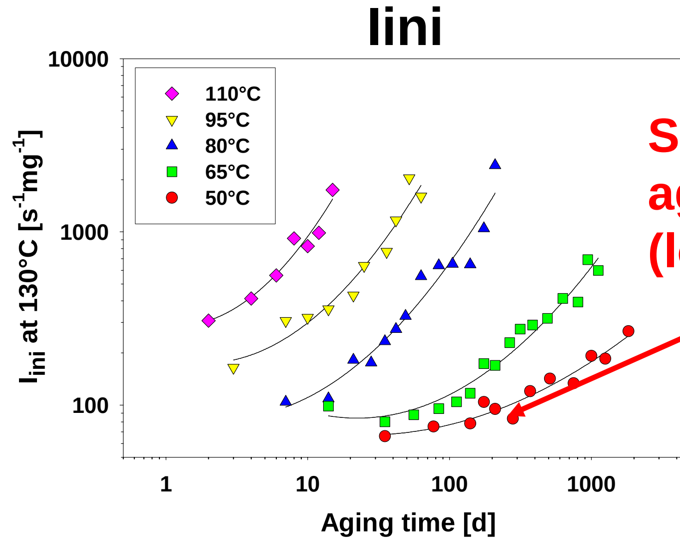
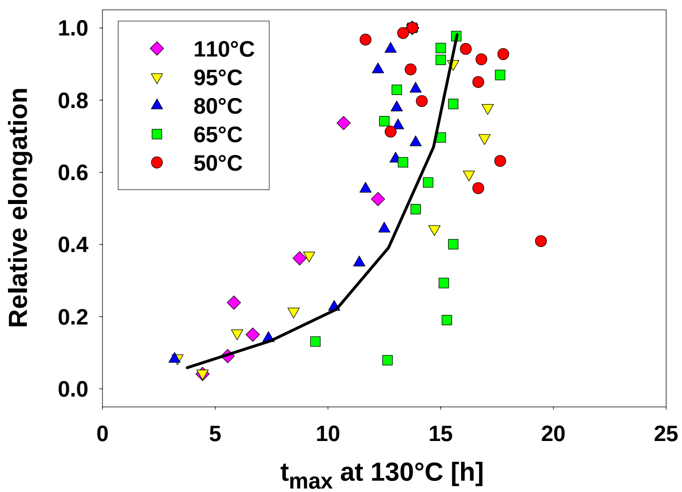
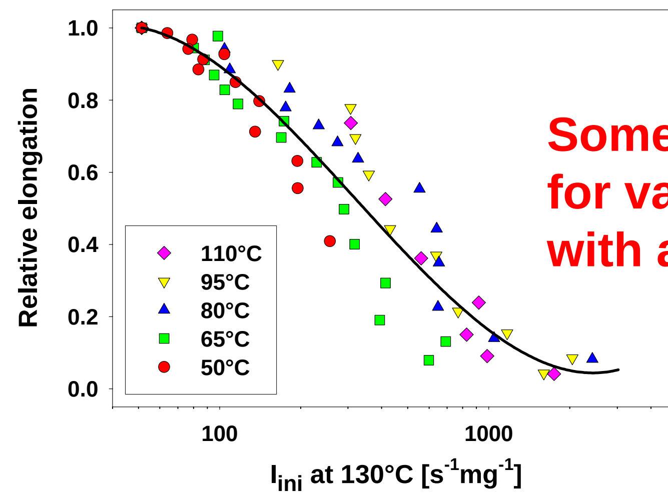
CL condition monitoring of aged HTPB material





Sensitivity to aging at 50°C (log scale !)





Some evidence for variations with aging T

- Observe shorter times to CL maximum with previous aging
- Sensitive increase in initial rate with previous aging

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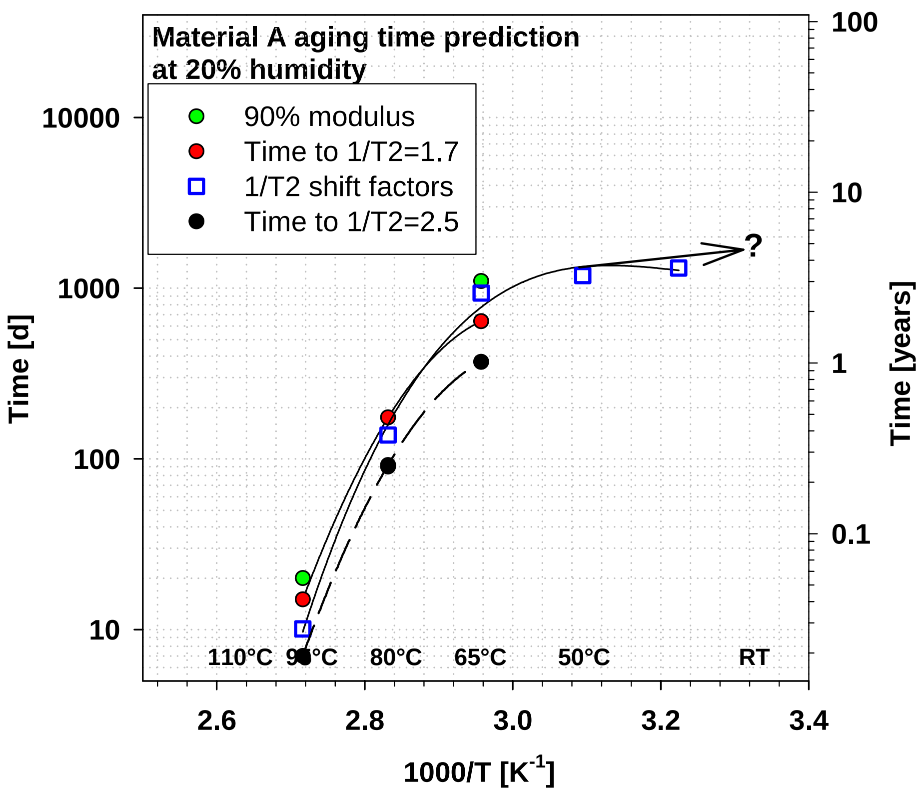
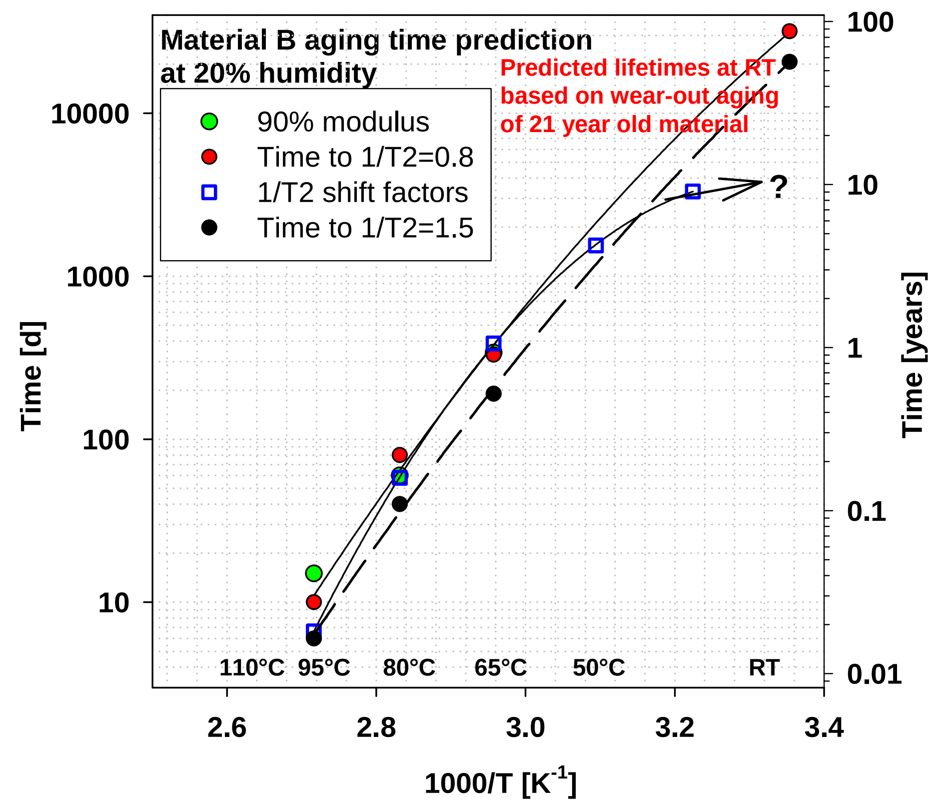
Example: Combined hydrolytic and thermal aging

- 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





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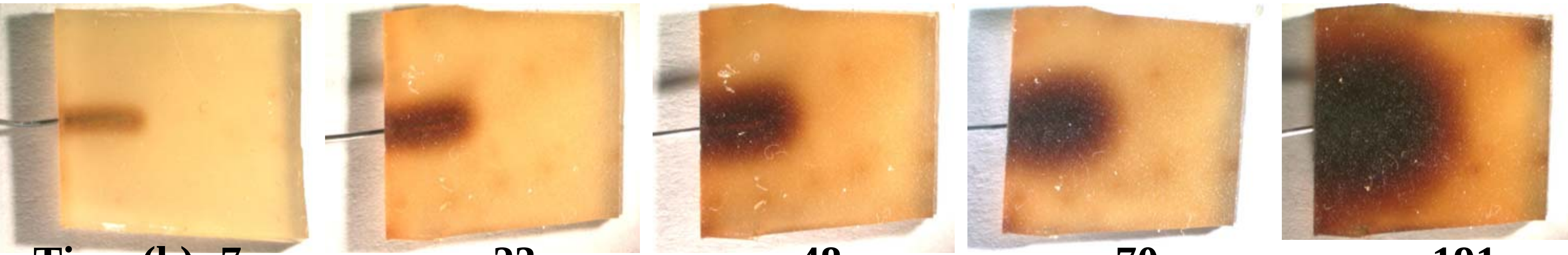
Oxidation spreading – heterogeneity – metal catalysis

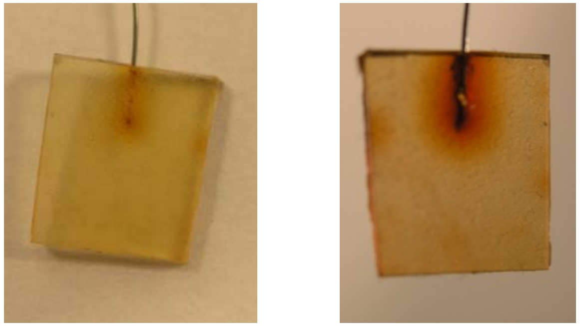
- Tinned copper wire, copper is a well-known catalyst
- Example of localized degradation

BPAN 95ºC



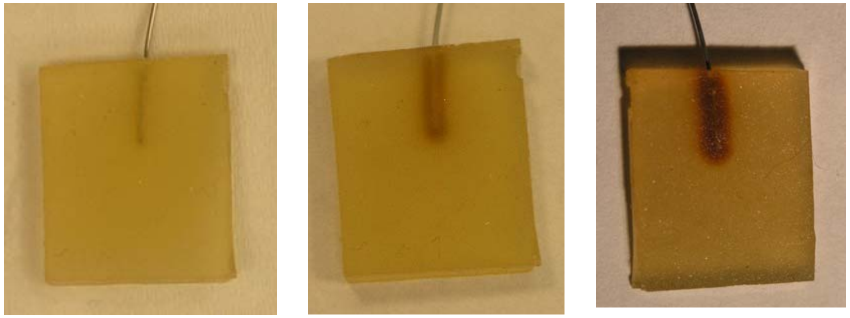
Time (h): 7 23 48 70 191

HTPB 50°C



2180h 11600h

PBAN RT



670h 3600h 12400h

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

A few conclusions

Temperature effects are well-known and important for:
DLO conditions during accelerated aging
Mechanistic variations for combined radiation-thermal aging

Observed non-linear behavior with T:
Oxygen consumption measurements for many materials
AO consumption features and correlation with failure
Wear-out studies of previously aged elastomer materials

- **Understand your materials and aging conditions as best as possible to conduct meaningful accelerated aging tests!**

Acknowledgements

Thanks for collaboration and a creative team environment are due to:

Ken Gillen, Roger Assink, Roger Clough, Leanna Minier, Julie Skutnik

Many years of DOE/DoD funding:

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Upcoming conference:

Previous ACS meetings, Chicago (1993), San Diego (2001)

2007 Spring NATIONAL ACS MEETING, CHICAGO (March 25-30, 07)

Deadline for Abstracts and Polymer Preprints: *t.b.a*, 2006.

Polymer Degradation, Optimization and Performance

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