SAND2007-3106C

ToF-SIMS Analysis of Oxidation Profiles in Elastomers

J. Ohlhausen, M. Celina, and M. Keenan

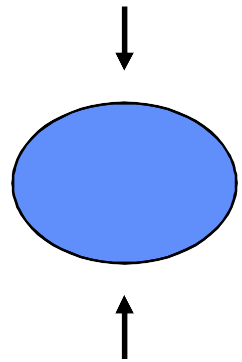
Friday, May 18, 2007

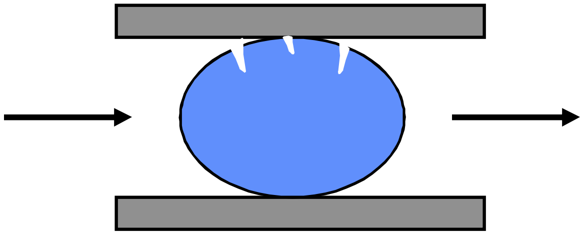
Tony Ohlhausen
jaohlha@sandia.gov

20 Annual SIMS Workshop
May 15-18, 2007
Key Largo, Florida

As Elastomers Age, Their Mechanical Properties Change

- Problems with Elastomer aging
  - O-ring lifetime reduction due to
    - Compression Set
    - Reduction in elasticity
    - Crack formation - embrittlement
- Consequences
  - Pressure stand-off is compromised
  - Leaks occur in pressure vessels
  - Controlled atmosphere lost





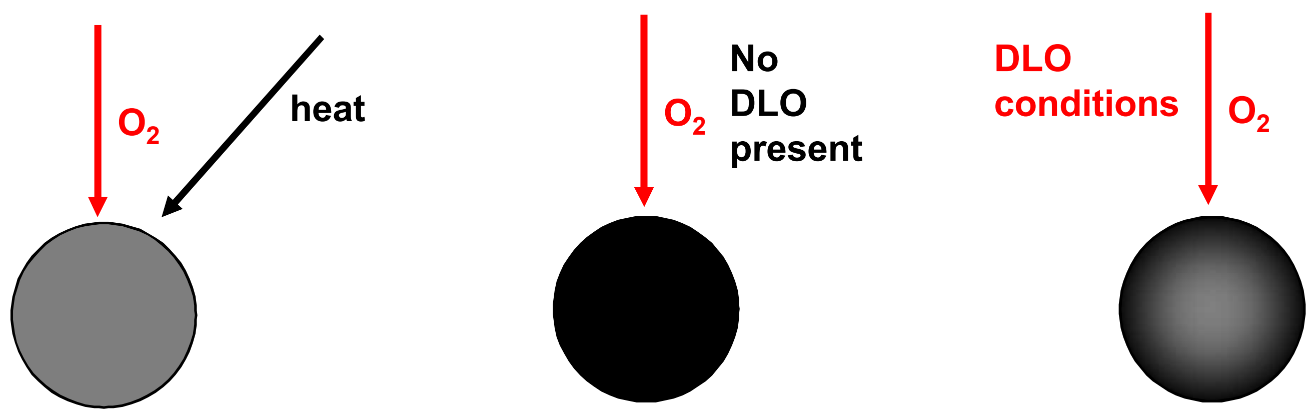
In order to reliably predict aging, we need to understand the processes that cause aging.

Sandia National Laboratories

Mandatory: Understand and eliminate DLO conditions for appropriate aging experiments

- 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**

O-ring cross section



Unaged o-ring

Uniform oxidation Through to bulk
Ambient slow aging

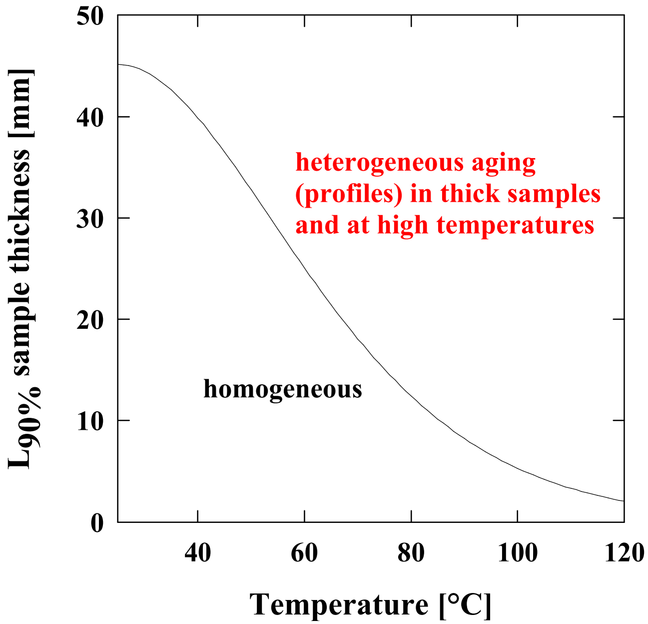
Oxidation only partially within top layer
Accelerated aging test

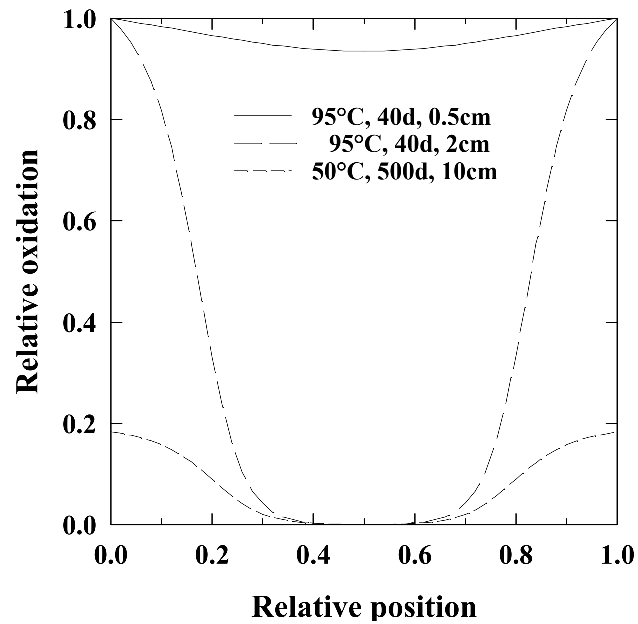
Measure or estimate *Φ* and *P* prior to conducting any accelerated aging tests!

Sandia National Laboratories

DLO modeling, development of heterogeneity

Thickness of non-diffusion limited oxidation (90% homogeneous)





- **Oxidation profiles can be modeled**
- **Requires knowing O_2 permeability and oxidation rate**
- **Models need to be validated with experimental data**

$$L_{90\%} = \sqrt{\frac{\alpha_c\, p\, P}{(\beta + 1)\,\phi\;\; 22400\,\delta}}$$

$$\alpha_c = \sim 2.5 \text{ for } \beta = 1; \alpha_c = 70 \text{ for } \beta = 10$$

p = partial pressure at surface [cmHg]
P = permeability [ccSTP/cm - s - cmHg]
ϕ = consumption rate [mol/g - s]
δ = density [g/cc]

Ken Gillen, Dept. 1821

J. Wise, K. Gillen, R. Clough, *Polymer, 38* (1997) 1929
M. Celina, A. Graham, K. Gillen, R. Assink, and L. Minier, *Rub. Chem. Tech., 73* (2000) 680

Sandia National Laboratories

Many Techniques Used to Probe Degradation Profiles

- Physical properties
- Hardening, modulus profile
- Density profiling
- Pin-point DMA
- AFM techniques
- Nano-indenters (Hysitron)

- Degradation chemistry
- FTIR, microtoming
  black samples difficult
- Micro- ATR IR
- CL imaging
  (limited to some polymers)
- NMR imaging (resolution)
- Surface techniques on cross-sections
  - XPS and XPS imaging
  - TOF-SIMS and SIMS imaging

No single technique provides all the answers

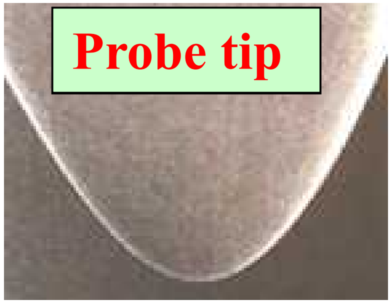
Correlations needed

Sandia National Laboratories

Physical Properties: Modulus profiling

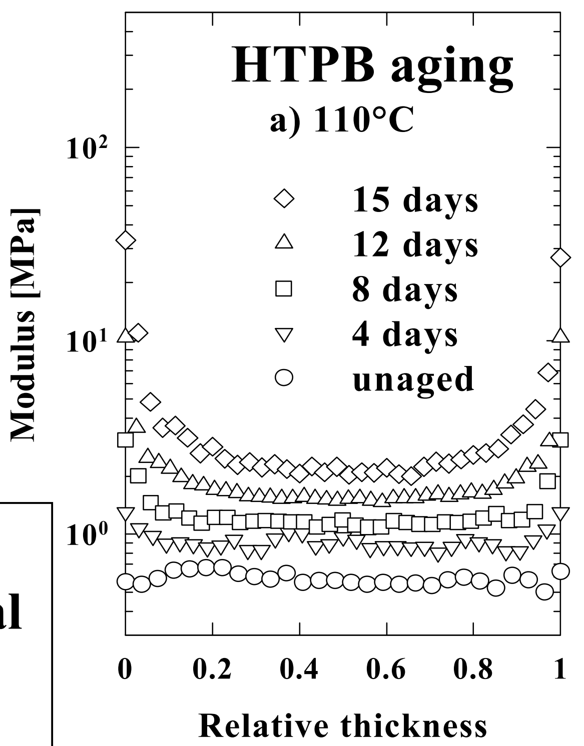
- Probing heterogeneous degradation effects, DLO profiles
- Parabolic micro indentation, two step load method
- Measures penetration under variable load, thermal and radiation aging

Modulus profiler



Probing of 2mm sample (40µm resolution)

- Resolution is limited
- Correlation between mechanical properties and degradation chemistry is needed



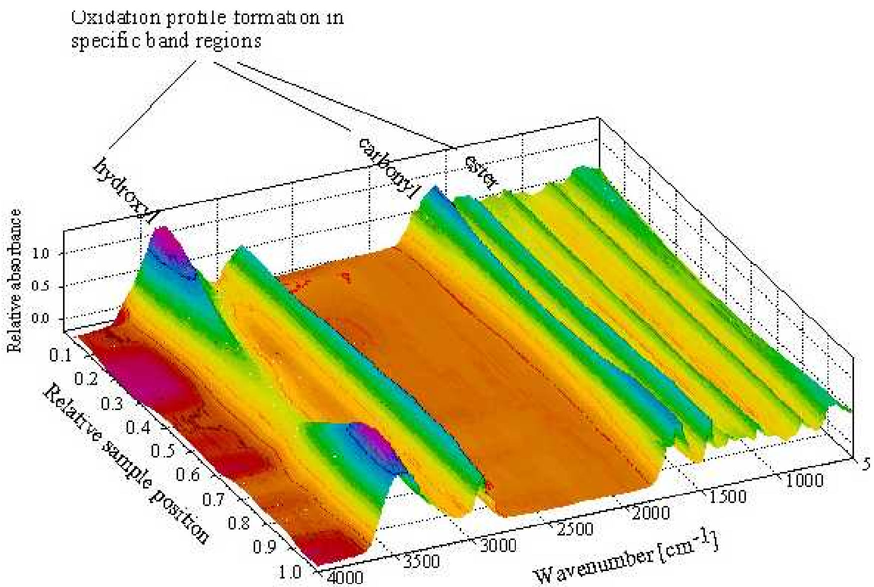
Ken Gillen, Dept. 1821

K. Gillen, E. Terrill, R. Winter, *Rub. Chem. Technol., 74* (2001) 428

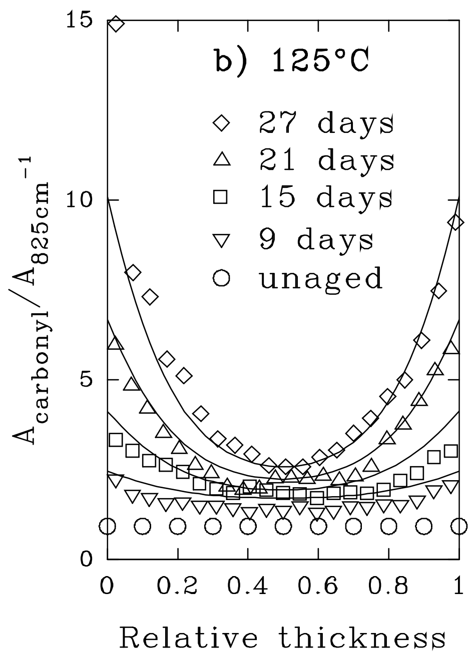
Sandia National Laboratories

Correlation of chemical and mechanical degradation

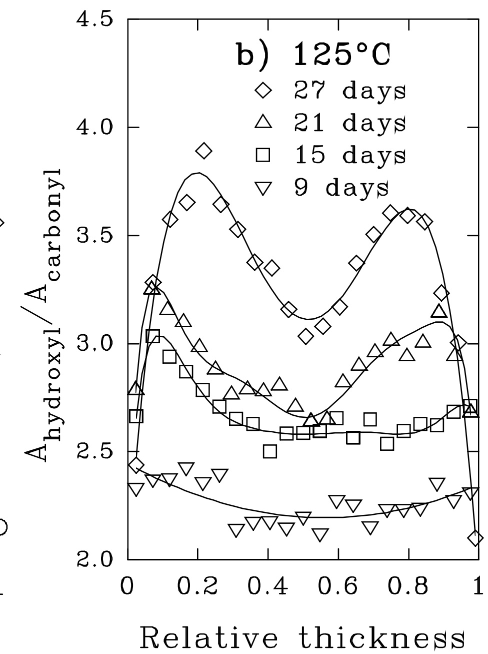
- Modulus profiling and FTIR microscopy (not usable for all materials)
- Some variations between bulk and surface degradation
- Good correlation between oxidation and elastomer hardening



Chemical degradation profile



Predicted modulus profile and carbonyl index

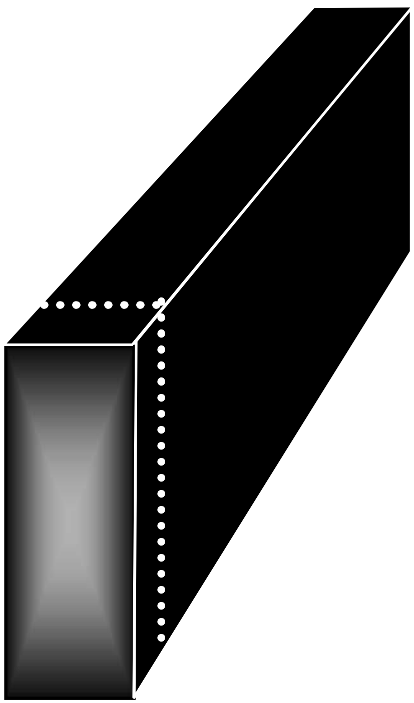


Edge complexity in hydroxyl

M. Celina, J. Wise, D. Ottesen, K. Gillen, R. Clough, *Poly. Deg. Stab., 60* (1998) 493
M. Celina, J. Wise, D. Ottesen, K. Gillen, R. Clough, *Poly. Deg. Stab., 68* (2000) 171

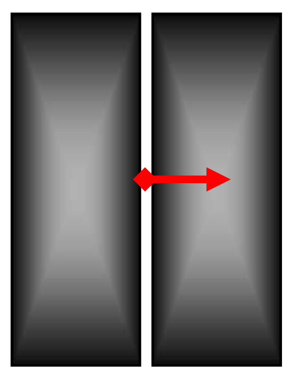
Sandia National Laboratories

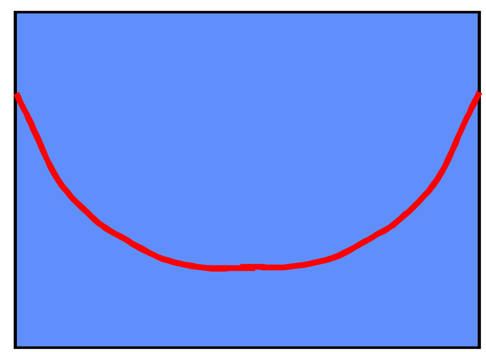
ToF-SIMS Sample Preparation and Analysis



^{18}O Aged
Accelerated aging:
(known time and temperature)

- Oxidize in controlled ^{18}O atmosphere
- Clean Sample (remove silicones)
- Section Sample
  - Cleaned and sharpened razor blade
- Place two pieces side-by-side in holder
- Perform line scan analysis halfway across sample in negative ion mode
  - 30x30μm per spectrum
  - 10μm between spectra
- Physical Electronics TRIFT I with ^{69}Ga Source

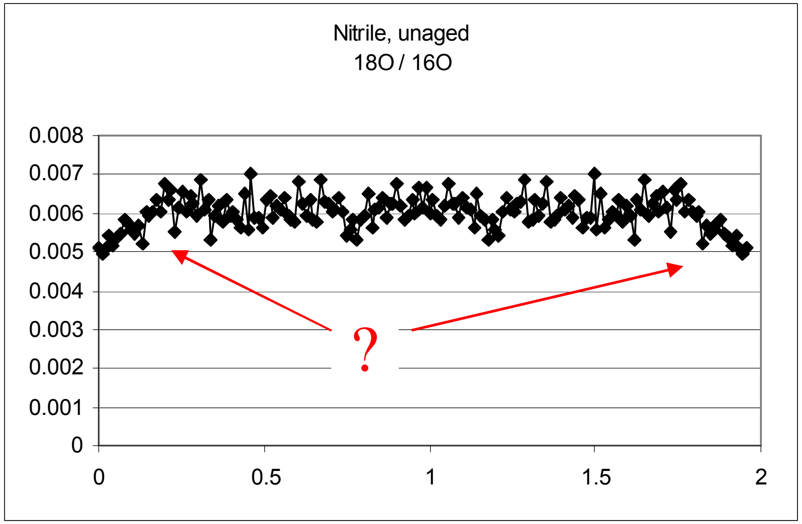


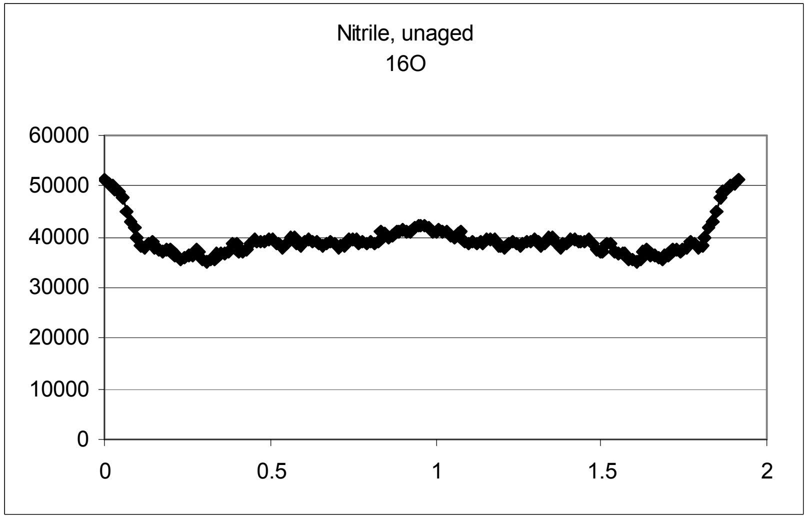


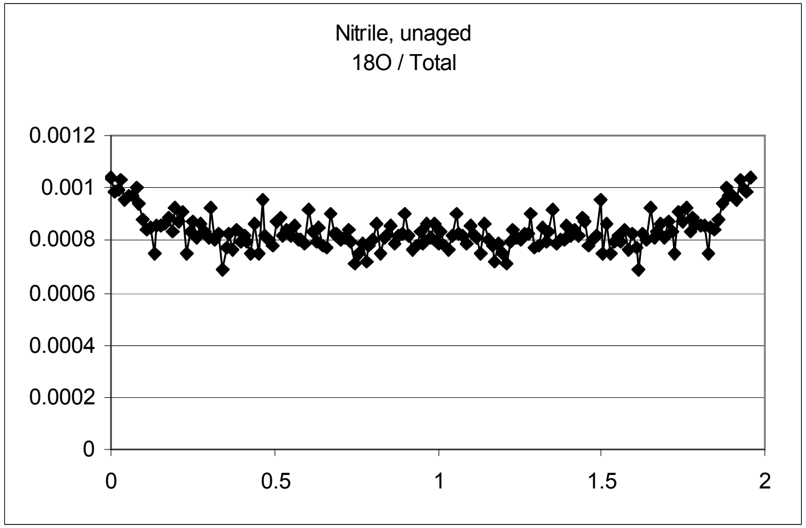
^{18}O profile

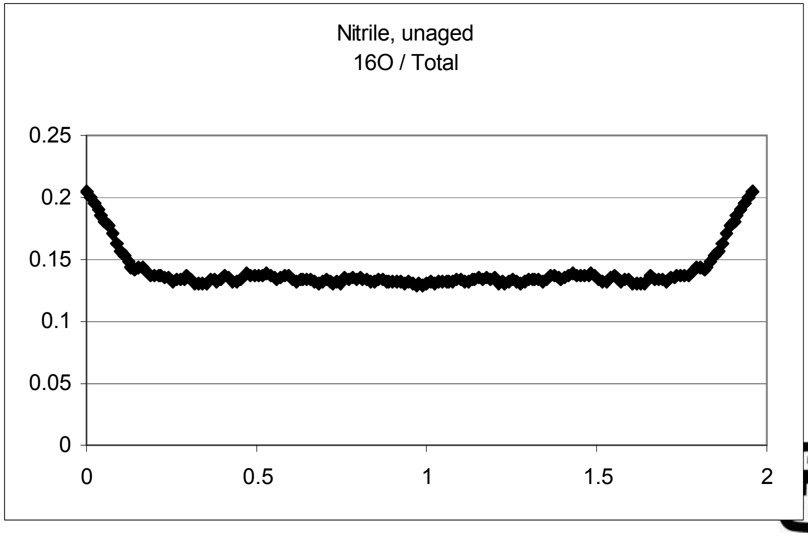
Sandia National Laboratories

Appropriate Signal Must be Used to Probe Oxidation Profile

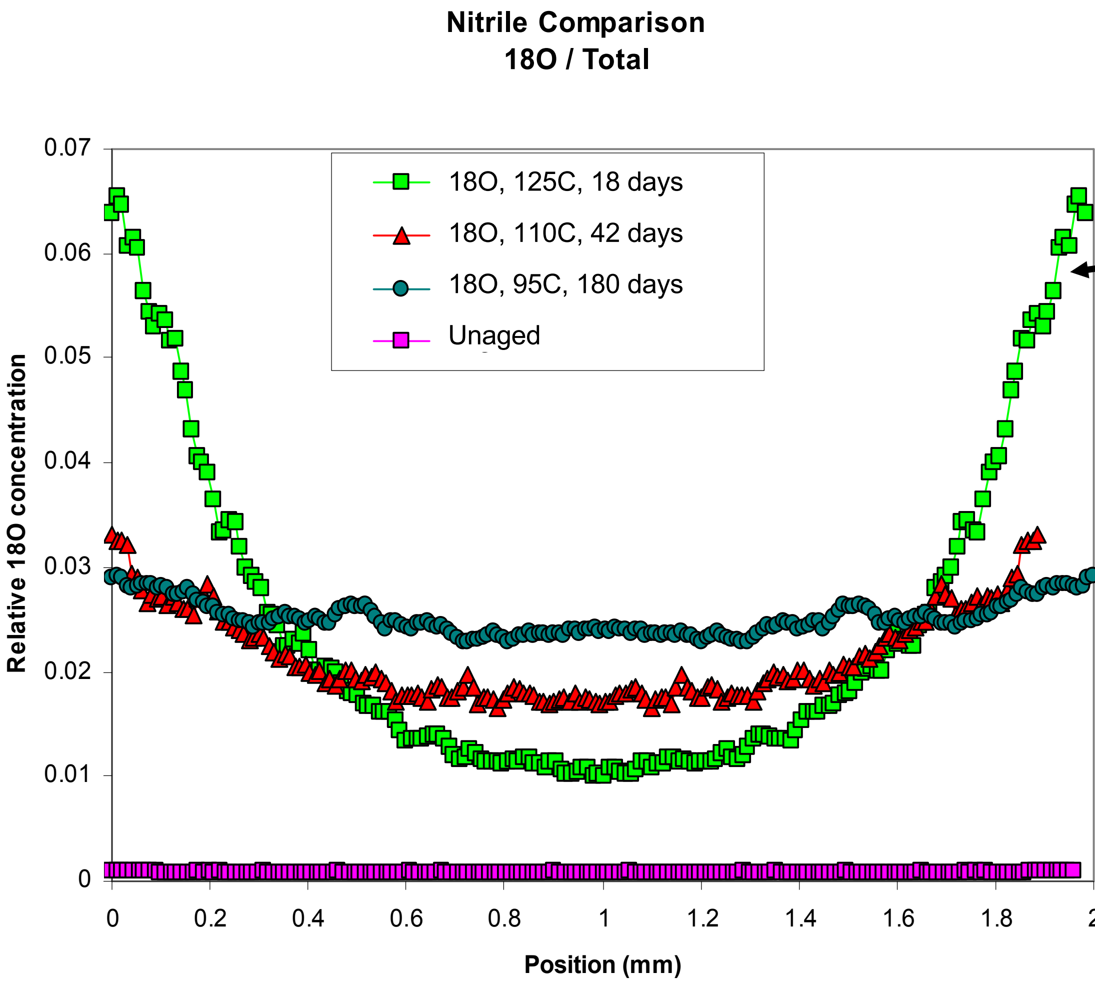








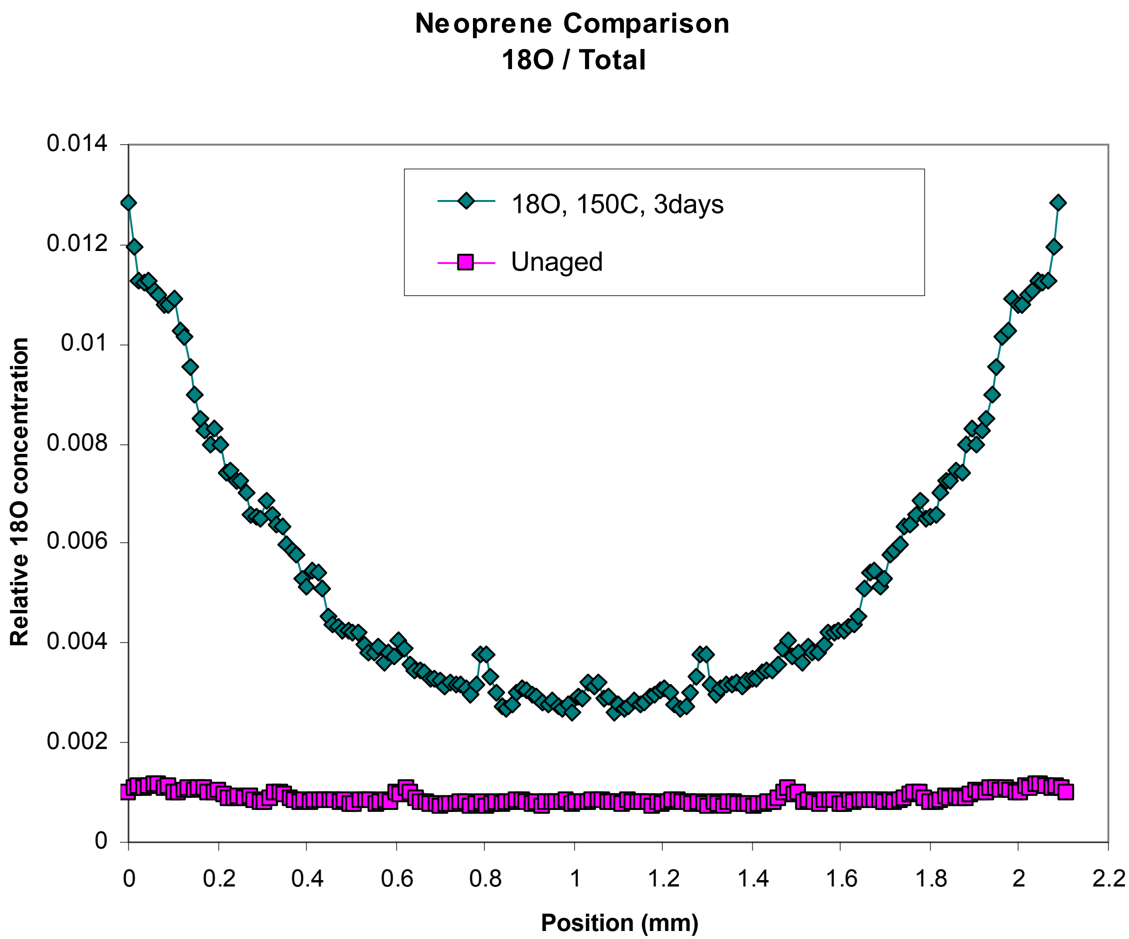
Filled Nitrile Aged in ^{18}O



- See expected trends:
- High temperatures lead to high ^{18}O concentrations at edge
- Long durations increase bulk ^{18}O concentrations
- Low ^{18}O concentration in unaged specimen

Sandia National Laboratories

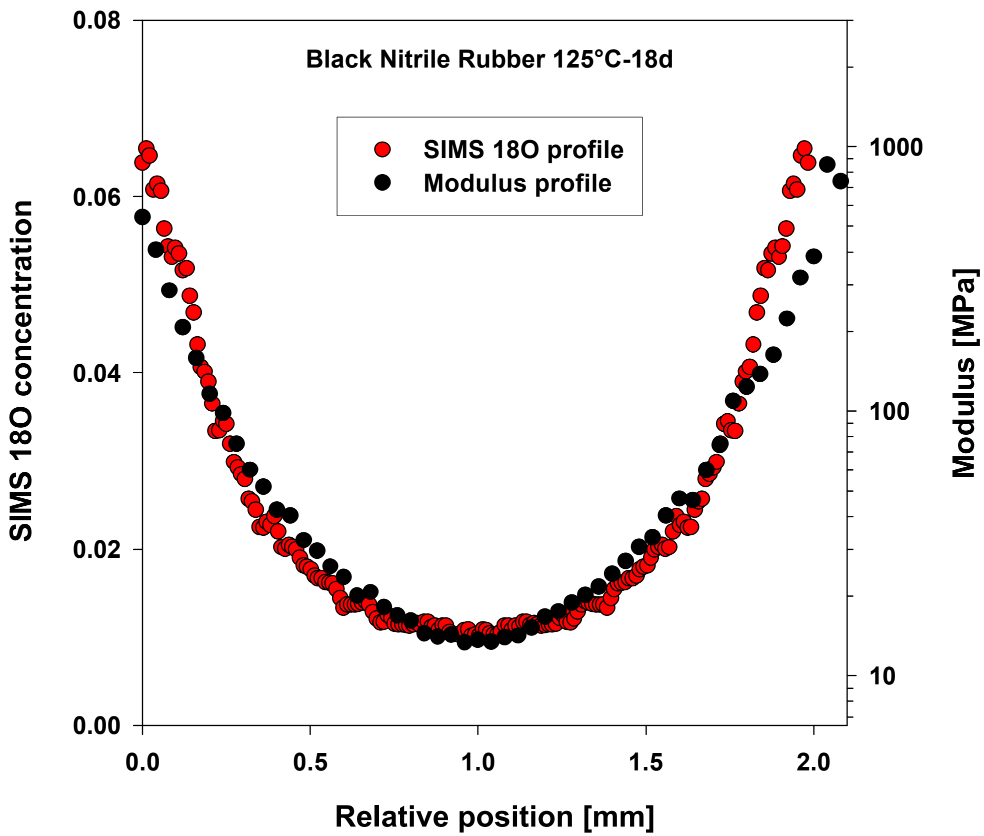
Filled Neoprene Aged in ^{18}O



- Note: These are filled elastomers (carbon and inorganic fillers)

- Other chemical techniques have difficulty acquiring good quality data from filled elastomers.

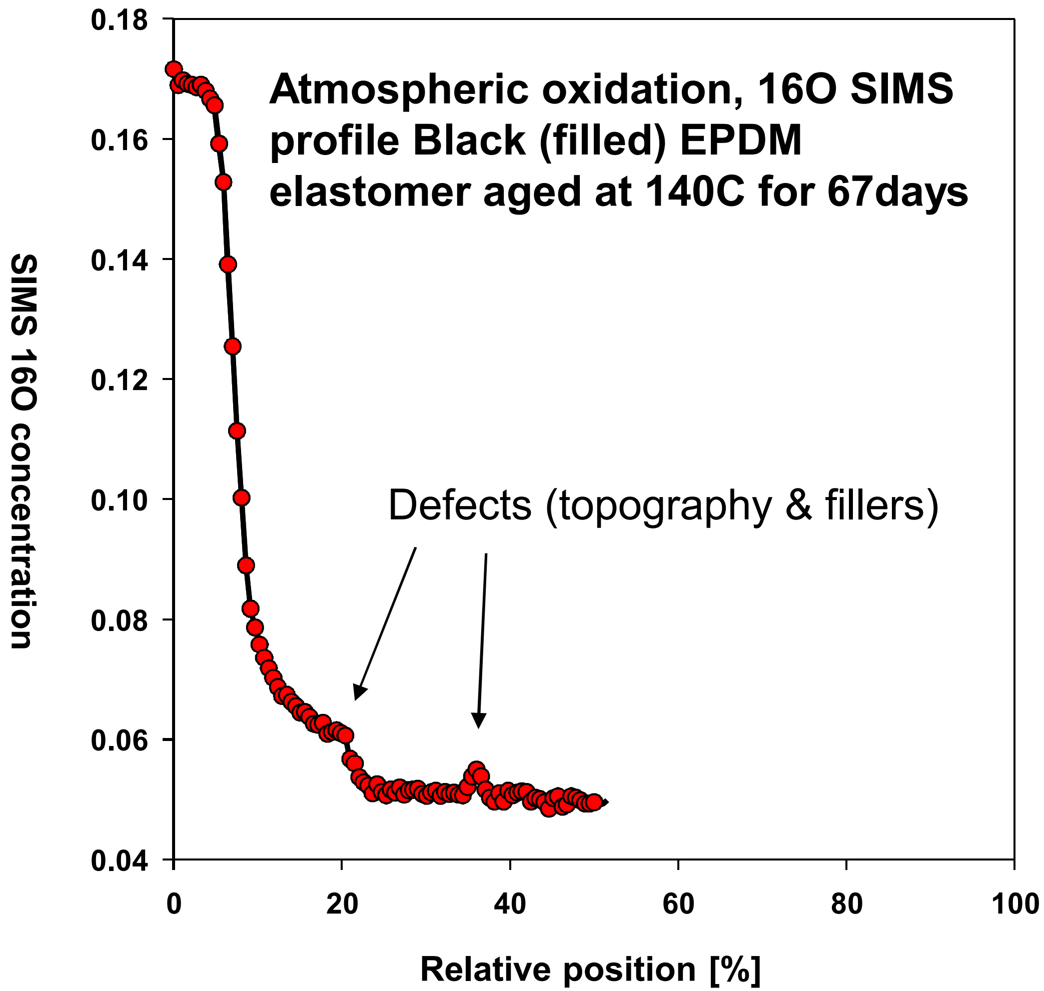
Correlation of mechanical and chemical measurement



- ToF-SIMS profiles correlate well with modulus measurements
- Data are consistent with models
- Degradation chemistry drives hardening.

Can use ToF-SIMS signal as guidance for mechanical properties.

Air-aged elastomers can also be analyzed using this method – much more difficult



- Steep U-shaped profile, induction time and rapid degradation starting at edges
  - Saturated on edges (real)
  - Very diffusion limited
  - High natural ^{16}O (from crosslinker and fillers)

Important to overcome presence of natural ^{16}O concentrations

Conclusions

- Using isotopically labeled oxidation, intentional oxidation can be separated from natural oxidation
- ToF-SIMS can be used to probe oxidation profiles of elastomers
  - ToF-SIMS works well on filled (real world) elastomers
  - Compared to alternate analyses, ToF-SIMS is quick analysis (4hrs for line scan)
  - We have shown that ToF-SIMS profiles correlate well with modulus profiles
- More work is needed to quantify data and to improve information content

Sandia National Laboratories

Future Directions

- Develop reliable quantification methods
- Use cluster source to improve large fragment yields
  - Investigate oxygen-containing fragment profiles
  - Perform multivariate analysis on data
- Repeat measurements on unfilled elastomers and compare to NMR and IR data
  - Charging problems in current ToF-SIMS instrument
- Acquire high quality imaging data to investigate the role of fillers in oxidation process.
- Develop better methods of cross-sectioning samples