

The Analysis of Oxidation Profiles in Elastomers Using ToF-SIMS

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AS+BI+NS-WeA, Rm. 610, 4:40pm

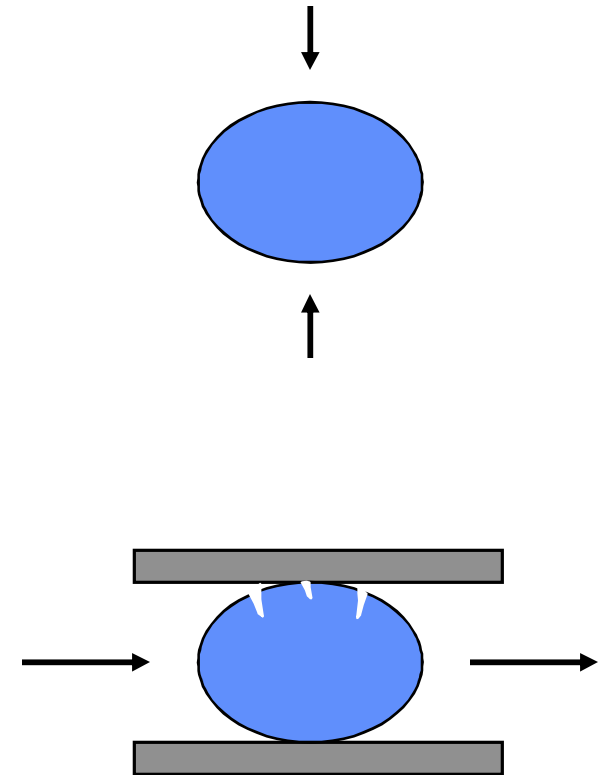
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As Elastomers Age, Their Mechanical Properties Change

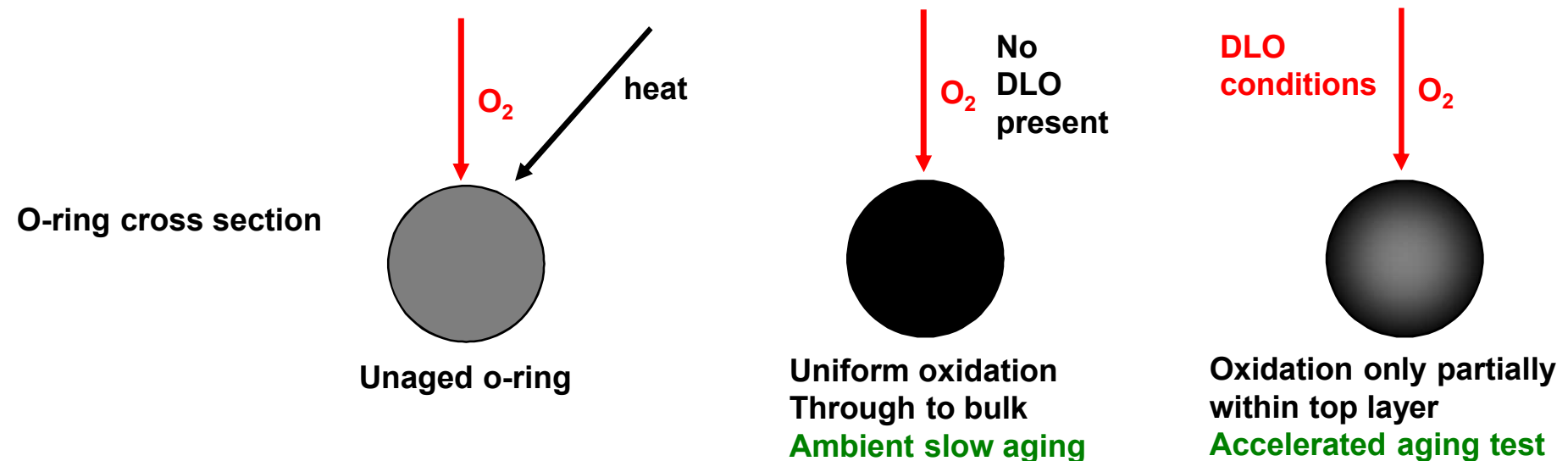
- **Problems with Elastomer aging**
 - O-ring lifetime reduction due to
 - Compression Set
 - Reduction in elasticity
 - Crack formation - embrittlement
- **Consequences**
 - Pressure stand-off is compromised
 - Leaks occur in pressure vessels
 - Controlled atmosphere lost



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

Mandatory: Understand and eliminate DLO conditions for appropriate aging experiments

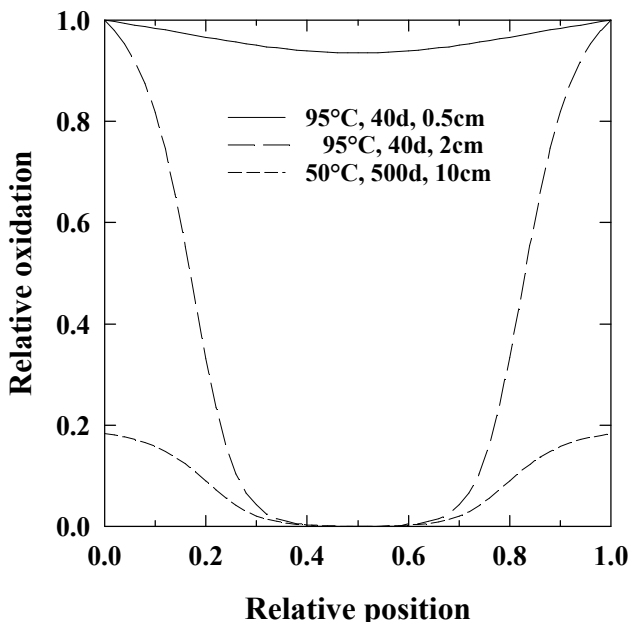
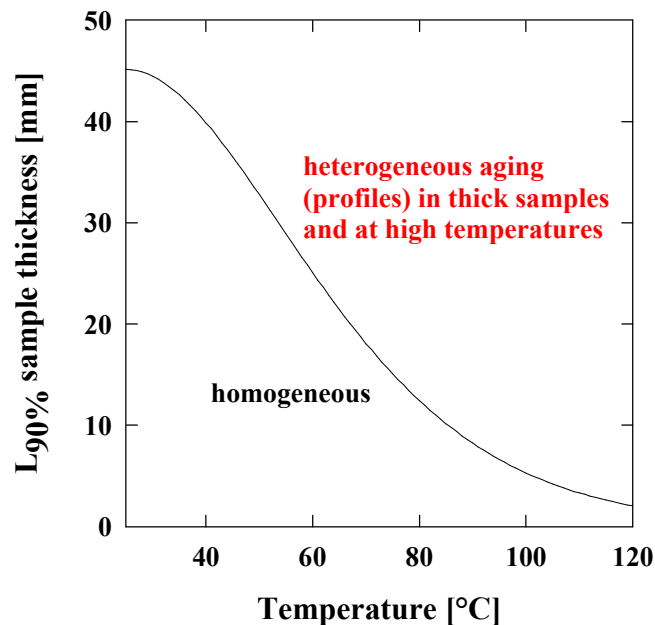
- DLO: Diffusion Limited Oxidation
- Oxidation in material is faster than oxygen can diffuse into it
- Will lead to oxidation profile formation, heterogeneous degradation
- Oxidation rate ϕ (consumption) versus permeability P (supply)
- Accelerated aging tests can completely misrepresent real aging



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

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

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

$\alpha_c = \sim 2.5$ for $\beta = 1$; $\alpha_c = 70$ 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]



Many Techniques Used to Probe Degradation Profiles

- Physical properties

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

No single technique
provides all the answers

- 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

Correlations needed



Physical Properties: Modulus profiling

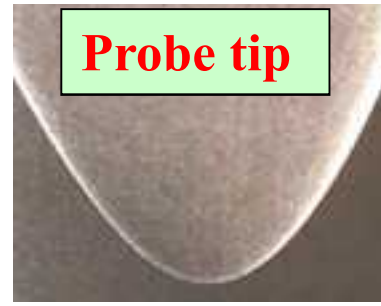
- Probing heterogeneous degradation effects, DLO profiles
- Parabolic micro indentation, two step load method
- Measures penetration under variable load, thermal and radiation aging



Modulus profiler

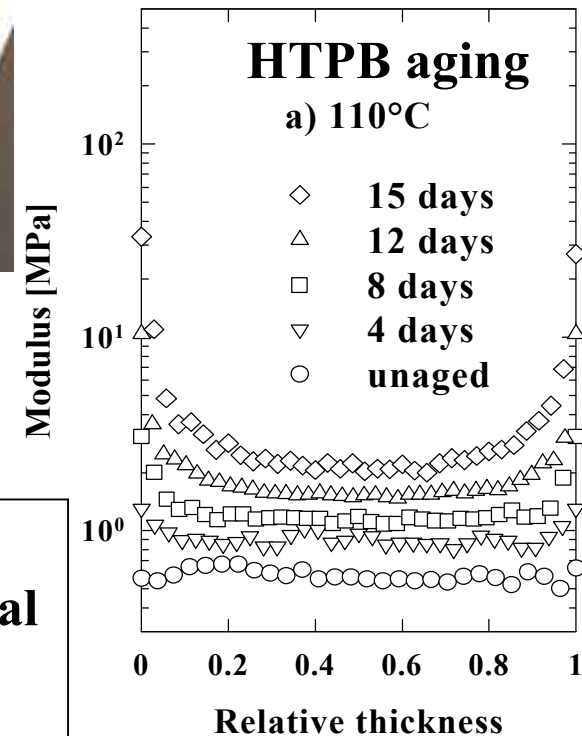


**Probing of 2mm sample
(40 μ m resolution)**



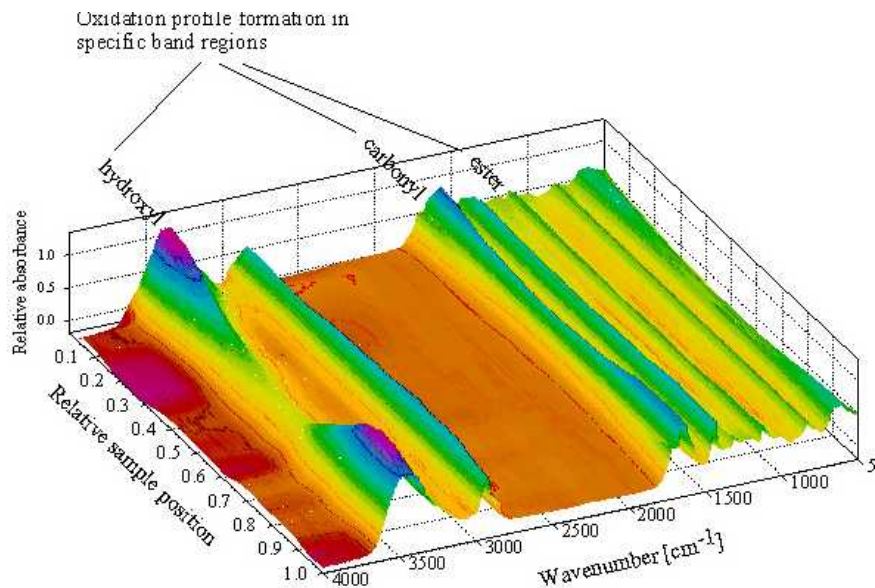
Probe tip

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

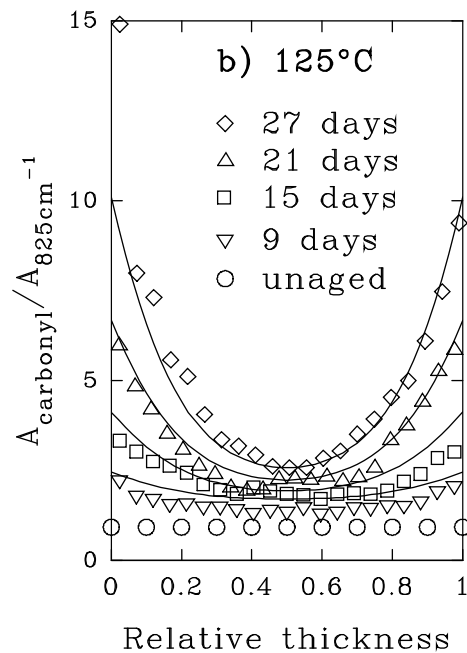


Correlation of chemical and mechanical degradation

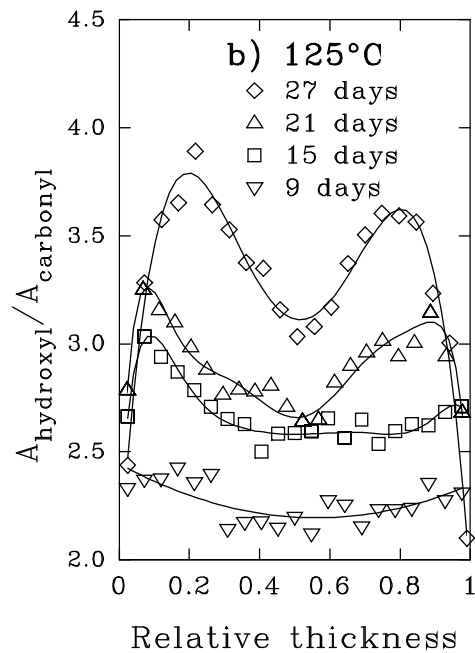
- Modulus profiling and FTIR microscopy (not usable for all materials)
- Some variations between bulk and surface degradation
- Good correlation between oxidation and elastomer hardening



Chemical degradation profile

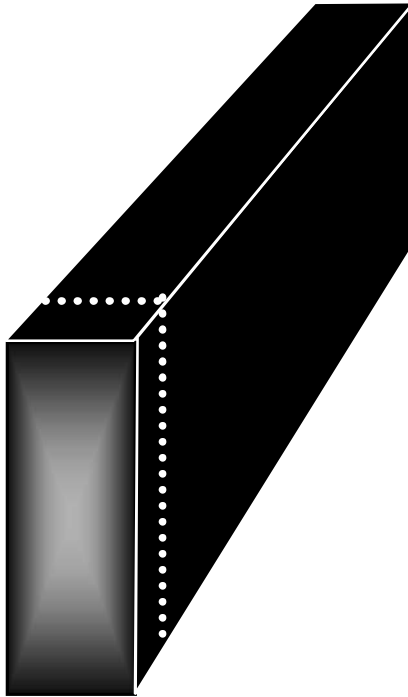


**Predicted modulus profile
and carbonyl index**



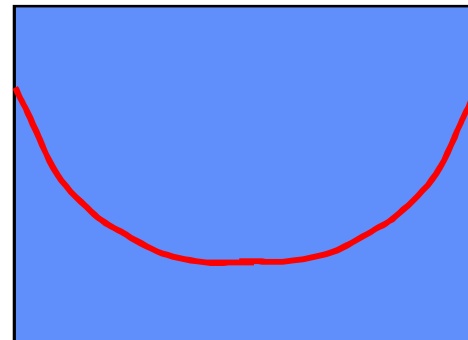
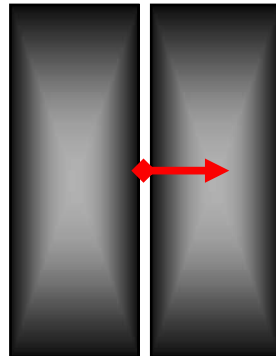
Edge complexity in hydroxyl

ToF-SIMS Sample Preparation and Analysis



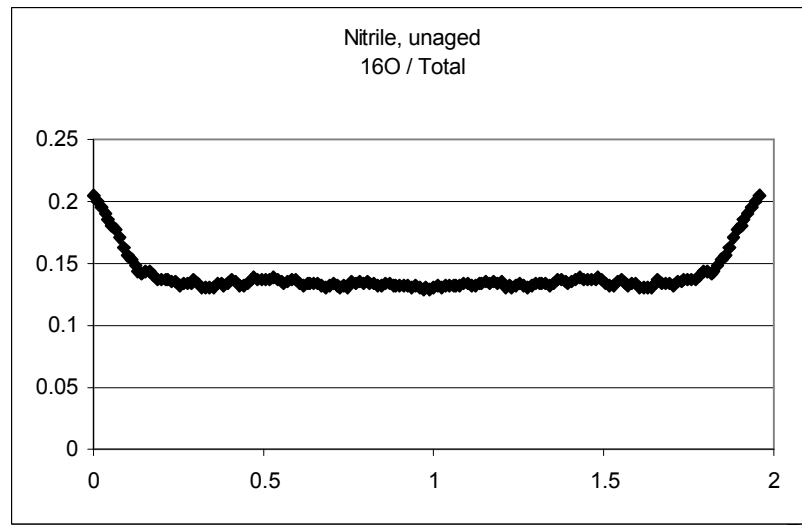
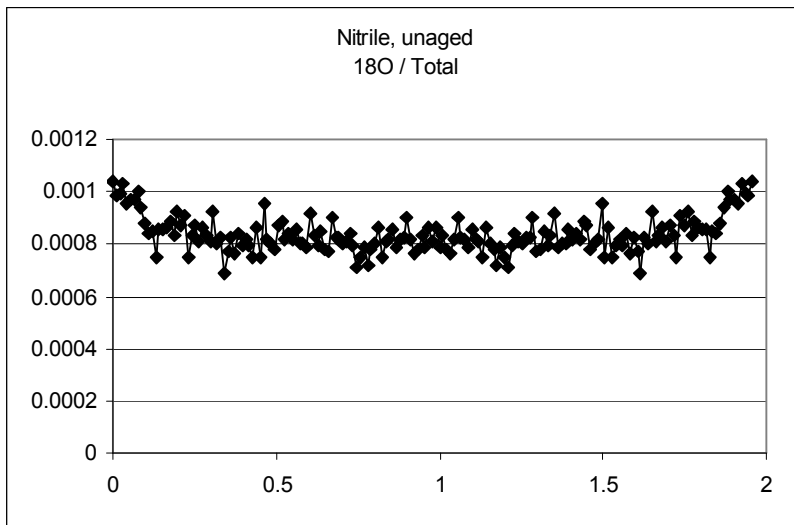
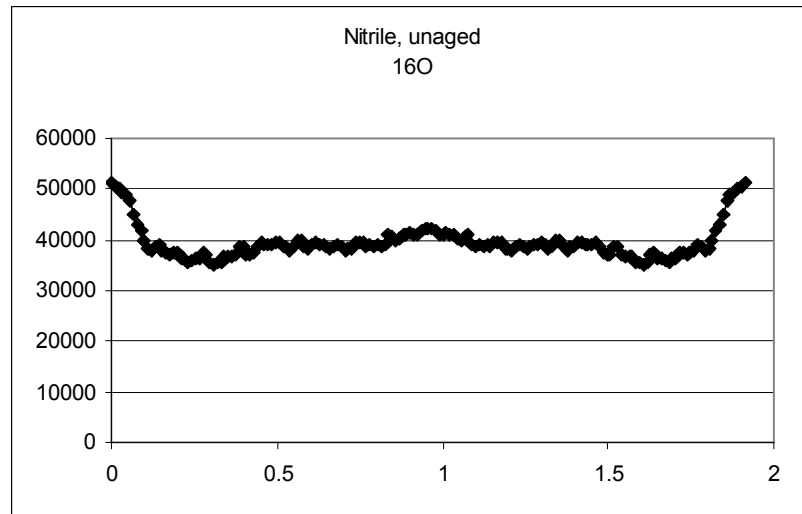
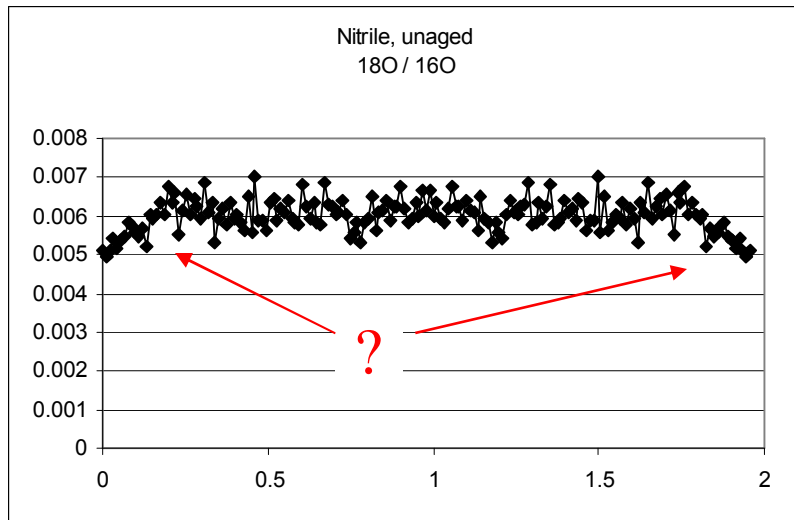
^{18}O Aged
Accelerated aging:
(known time and
temperature)

- 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
 - $30 \times 30 \mu\text{m}$ per spectrum
 - $10 \mu\text{m}$ between spectra
- Physical Electronics TRIFT I with ^{69}Ga Source



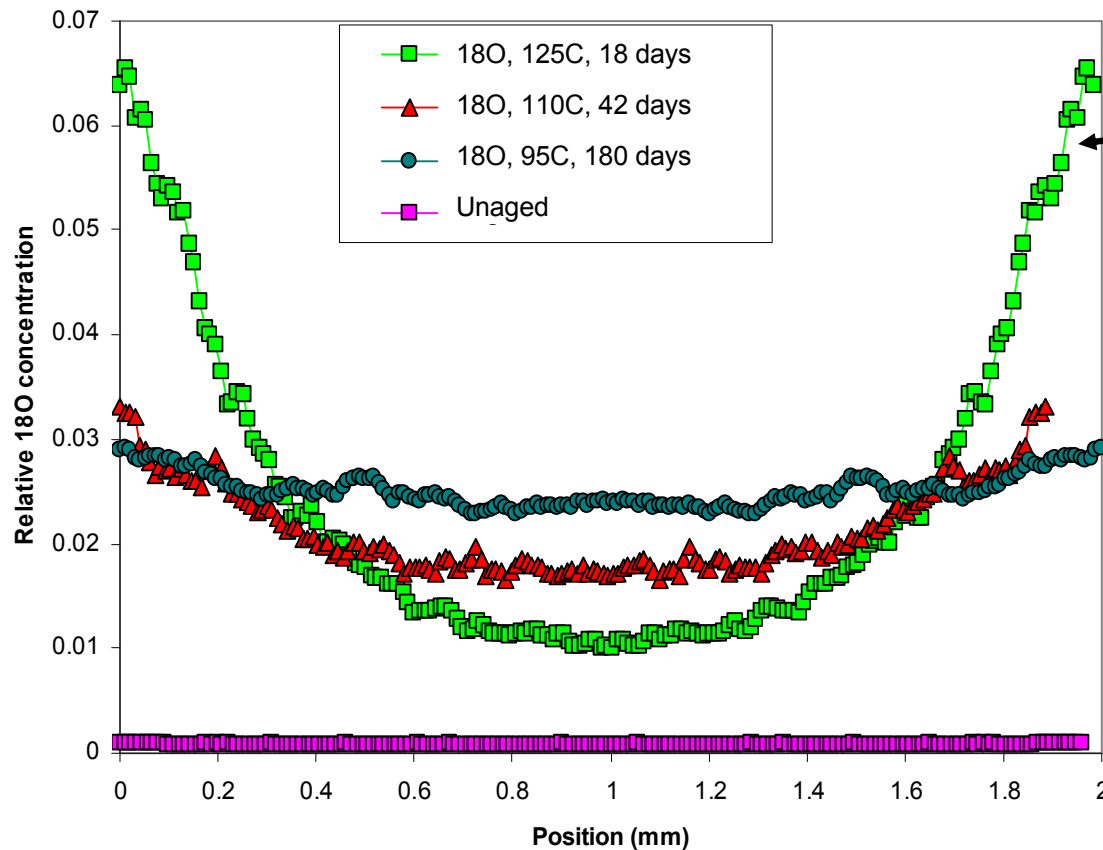
^{18}O profile

Appropriate Signal Must be Used to Probe Oxidation Profile



Filled Nitrile Aged in ^{18}O

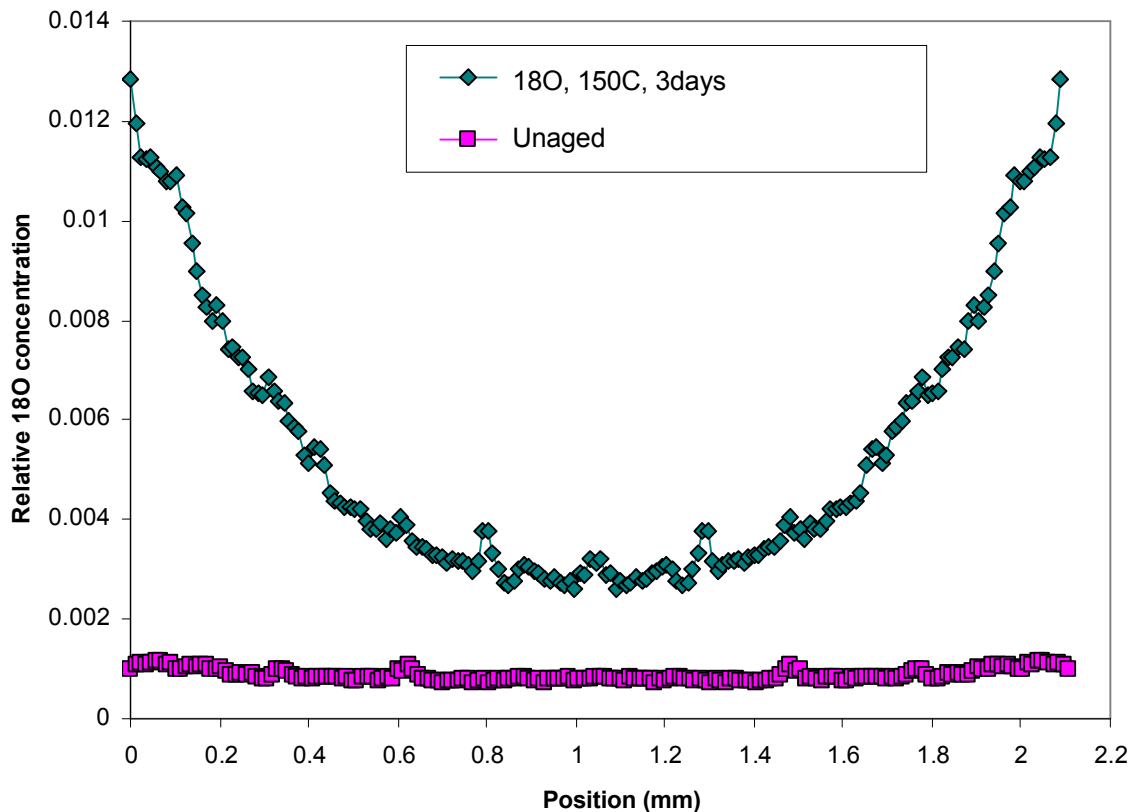
Nitrile Comparison
 ^{18}O / Total



- 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

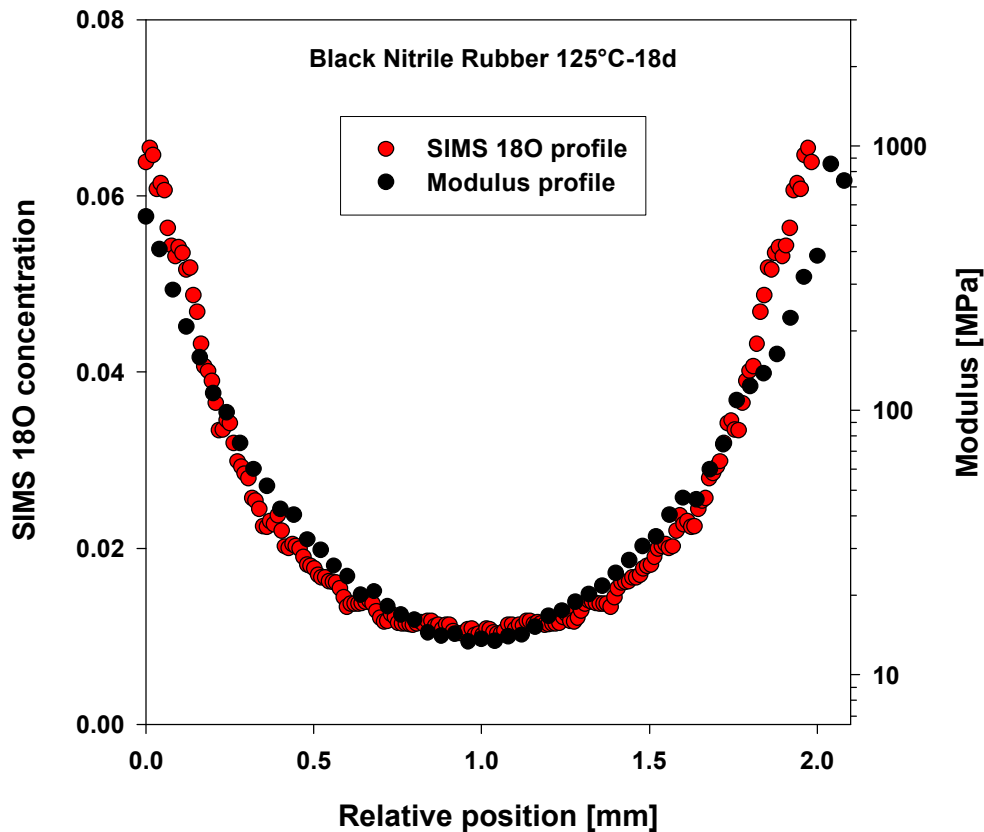
Filled Neoprene Aged in ^{18}O

Neoprene Comparison
 ^{18}O / Total



- Note: These are filled elastomers (carbon and inorganic fillers)
- Other chemical techniques have difficulty acquiring good quality data from filled elastomers.

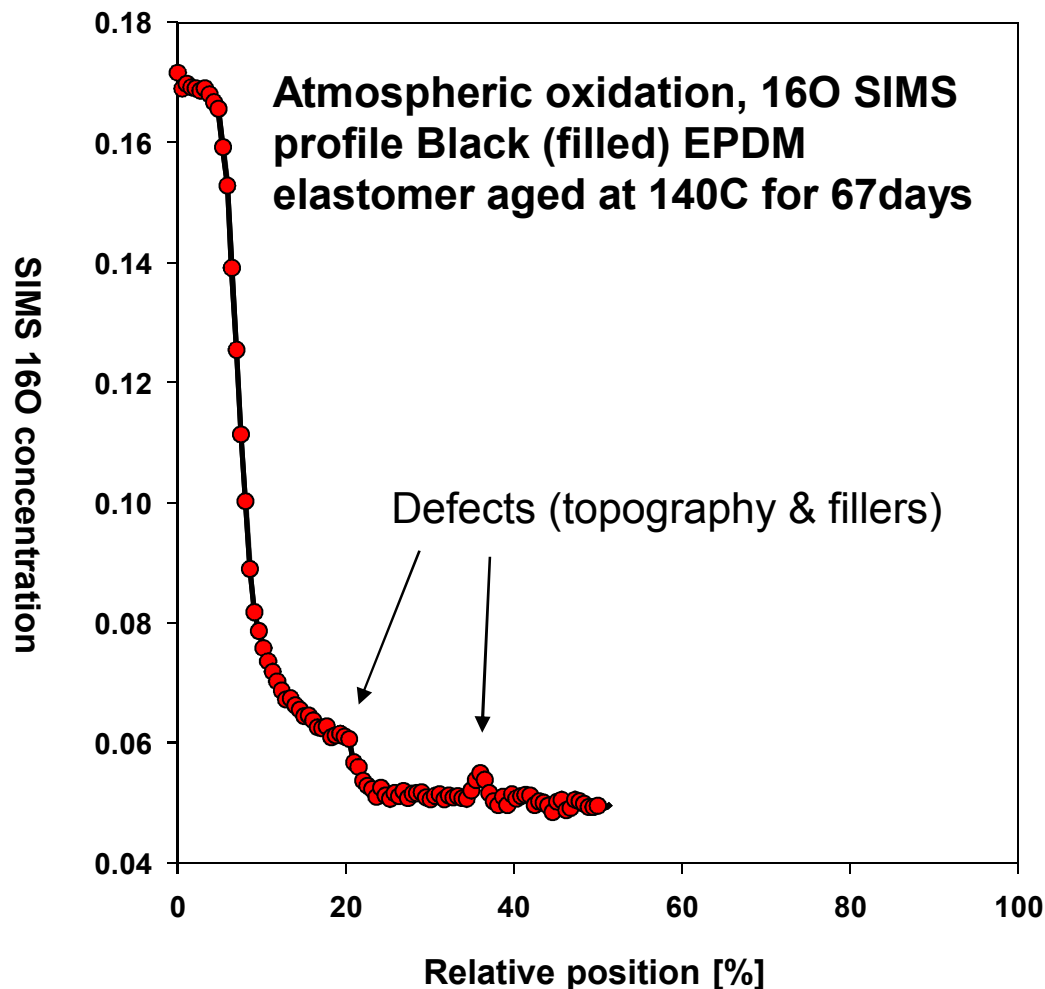
Correlation of mechanical and chemical measurement



- 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**



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**