SAND2015-7112C

Exceptional service in the national interest

Sandia National Laboratories



Pushing the thermal boundaries of polymers: some unexpected results

E. M. Redline[a], T. Pyatina[b], T. Sugama[b]

31 August 2015

U.S. DEPARTMENT OF ENERGY

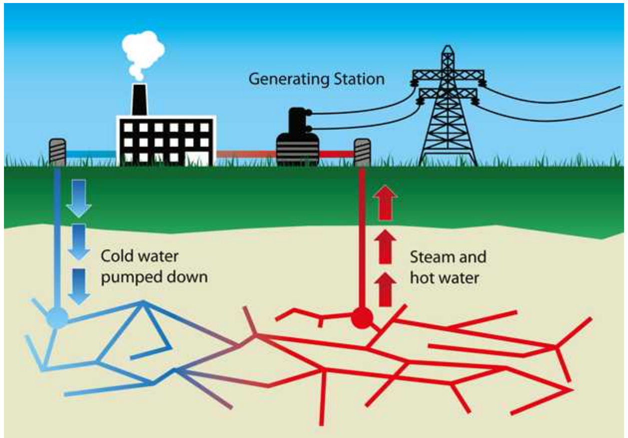
NNSA National Nuclear Security Administration

Sandia National Laboratories is a multi-program laboratory managed and operated by Sandia Corporation, a wholly owned subsidiary of Lockheed Martin Corporation, for the U.S. Department of Energy's National Nuclear Security Administration under contract DE-AC04-94AL85000.

[a]Sandia National Laboratories
[b]Brookhaven National Laboratory

A Bit of Background

- The desire to reduce reliance on fossil-based fuels has lead to research in renewable energy sources, e.g. geothermal.
- Industry is interested in elastomeric materials for use as seals, non-metallic pump bearings and other drilling components.
- Geothermal wells typically experience temperatures around 150°C, but there is a push to create wells with temperatures nearing 300°C. Pressures of 3000+ psi are common
- The initial project focused on evaluation of commercial-based elastomers in simulated geothermal environments to provide material selection guidance to industry.

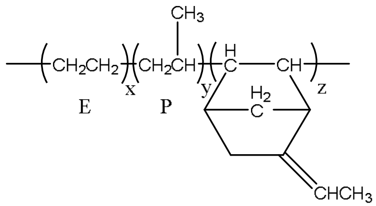


www.carbonneutral.com

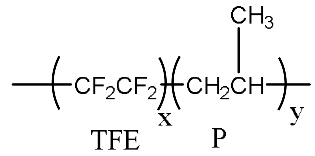
Experimental Set-Up

- Five elastomeric materials were purchased from Precision Associates, Inc.

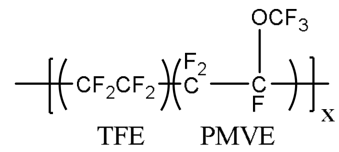
EPDM



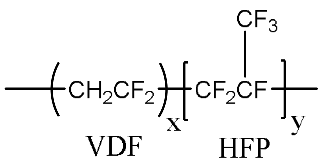
FEPM (e.g. Aflas®)



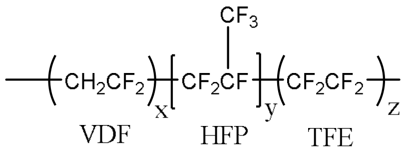
FFKM (e.g. Kalrez®)



Type I FKM (e.g. Viton® A)



Type II FKM (e.g. Viton® B)



- Materials were exposed to five environments:

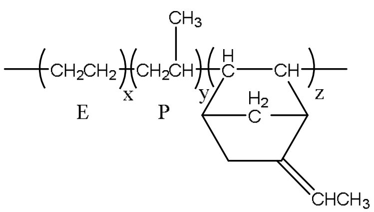
1. Thermal cycle (5 cycles: heat to 300°C in air, 1000 psi for 24 hr, quench to 25°C)
2. Aerated steam/cooling thermal cycle (5 cycles: heat to 300°C in air, 1000 psi for 24 hr, quench to 25°C)
3. Non-aerated steam/cooling thermal cycle (5 cycles: heat to 300°C in N_2, 1000 psi for 24 hr, quench to 25°C)
4. Drilling fluid (pH 9-10), 300°C, 7 days, 1000 psi
5. Brine (pH 4-5), 300°C, 7 days, 1000 psi

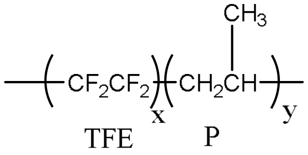
An Unexpected Result

- During the course of evaluation we noticed that EPDM and FEPM had poor resistance to thermal shock under oxidative conditions.

EPDM → thermal cycle*, air

thermal cycle*, air ← **FEPM**

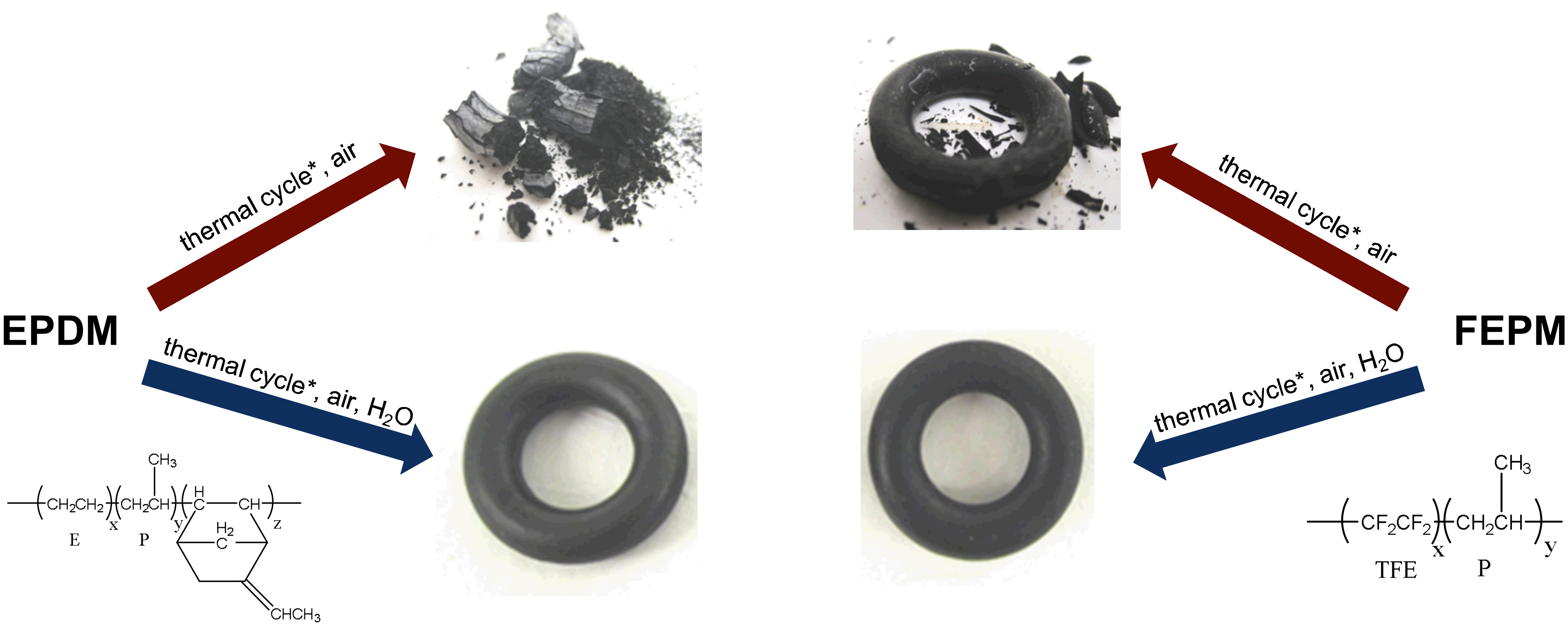




*thermal cycle = 5 cycles: heat to 300°C, 1000 psi for 24 hr, quench to 25°C

An Unexpected Result

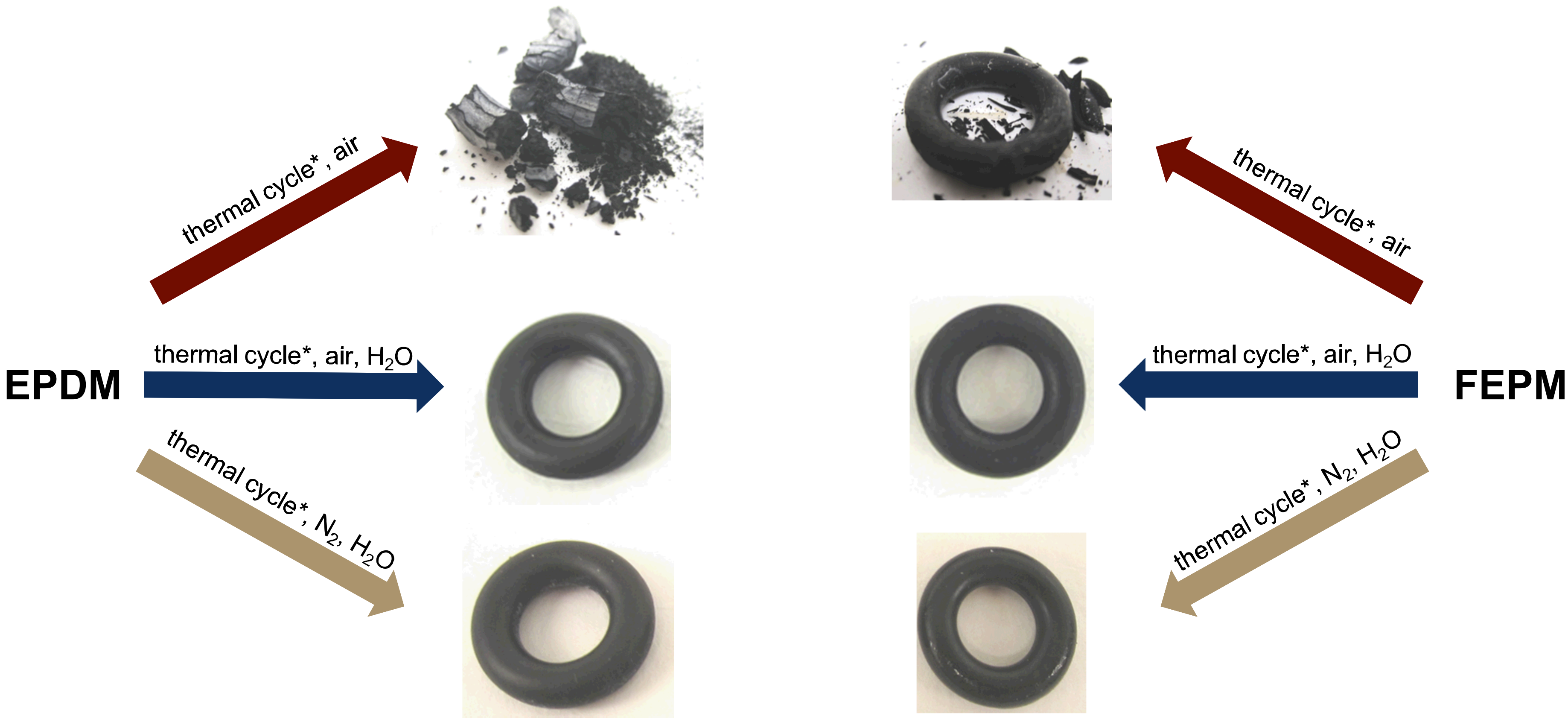
- During the course of evaluation we noticed that EPDM and FEPM had poor resistance to thermal shock under oxidative conditions.
- When steam was added during the thermal cycle test, the O-rings showed marked improvement in stability.



*thermal cycle = 5 cycles: heat to 300°C, 1000 psi for 24 hr, quench to 25°C

Pieces of the Puzzle - Visual

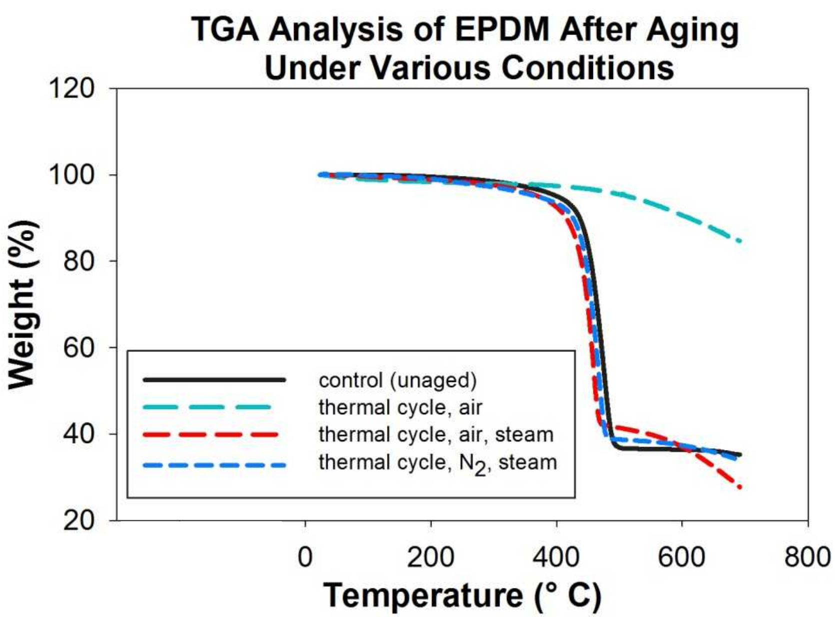
- EPDM and FEPM O-rings also appeared intact after thermal cycling in the presence of N_2 and steam.

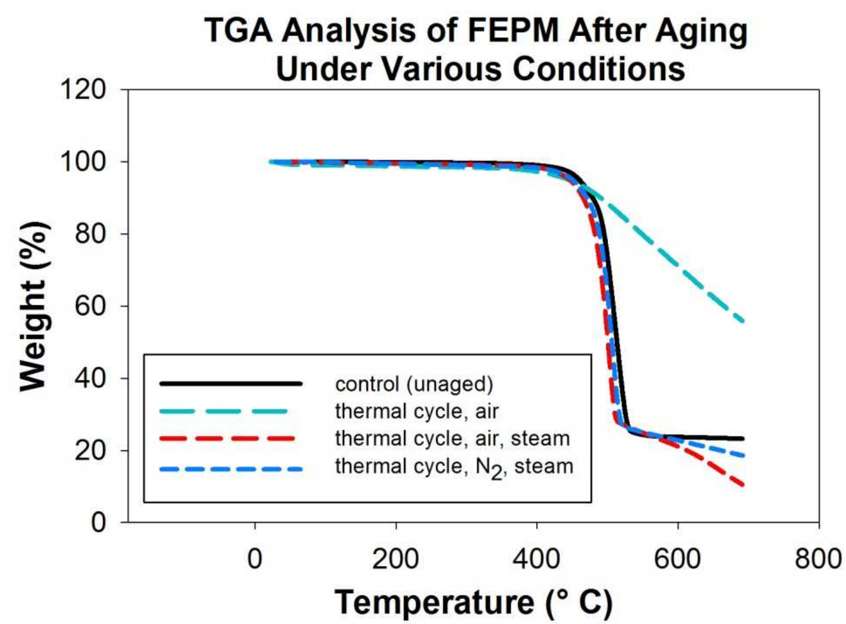


*thermal cycle = 5 cycles: heat to 300°C, 1000 psi for 24 hr, quench to 25°C

Pieces of the Puzzle – TGA

- Thermal stability of EPDM and FEPM in the presence of steam with either air or N_2 was similar to that of unaged.
- Thermal cycle tests revealed much slower decline in weight loss, likely due to the formation of carbonaceous compounds





Pieces of the Puzzle – TGA, Weight Loss

- Onset degradation temp for EPDM and FEPM: thermal cycle, N_2, steam > thermal cycle, air, steam, > thermal cycle, air.
  - Indicates thermal cycle in air had most damage and thermal cycle in N_2 least damage.
- Temp at max decomposition rate had small decline for both polymers.

Testing environment, EPDM	Onset Degradation Temperature (°C)	Temperature at Maximum Decomposition rate (°C)
Control	118	476
Thermal cycle, air	29	-
Thermal cycle, air, steam	44	458
Thermal cycle, N_2, steam	94	467

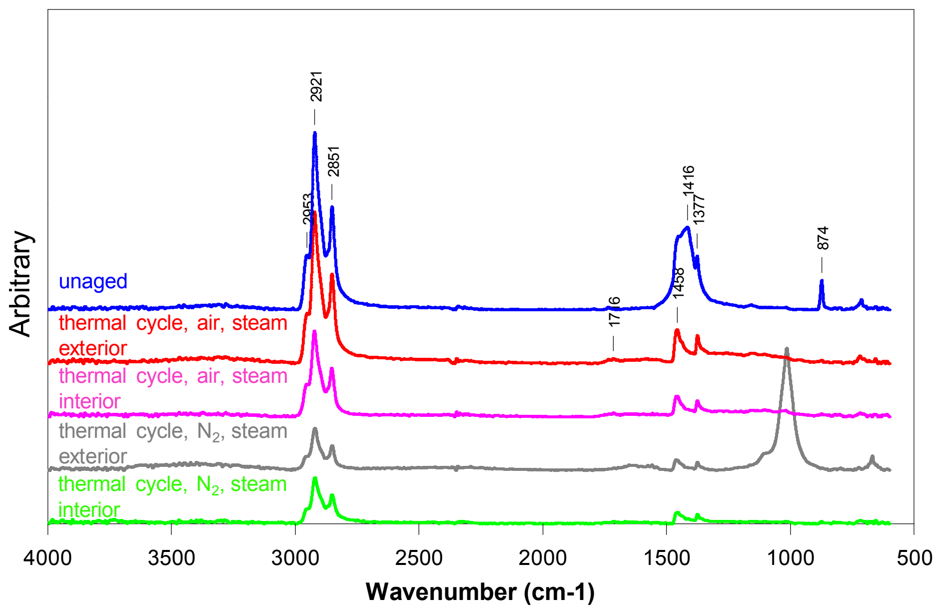
Testing environment, FEPM	Onset Degradation Temperature (°C)	Temperature at maximum decomposition rate (°C)
Control	152	514
Thermal cycle, air	27	507
Thermal cycle, air, steam	47	502
Thermal cycle, N_2, steam	54	506

Pieces of the Puzzle – FTIR

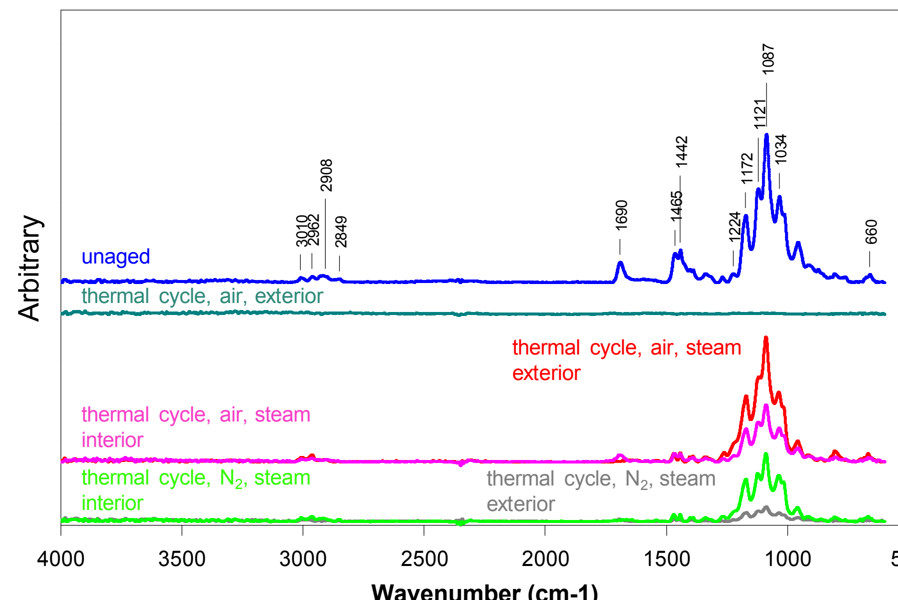
Sandia National Laboratories

- EPDM loses all characteristic bands after thermal cycling in air (not shown).
- EPDM: Appearance of carboxylate species (1530-1580 cm^{-1}) and carbonyl (1715 cm^{-1}) after steam/air thermal cycling.
- FEPM surface loses characteristic peaks after thermal cycling in air.
- FEPM reduction in: 2908, 2849 (C-H stretch) and 1465 (CH_3 bend), 1442 cm^{-1} (CH_3 bend or CH_2 scissor) after steam tests.

EPDM



FEPM



Pieces of the Puzzle – Oxidation Rates

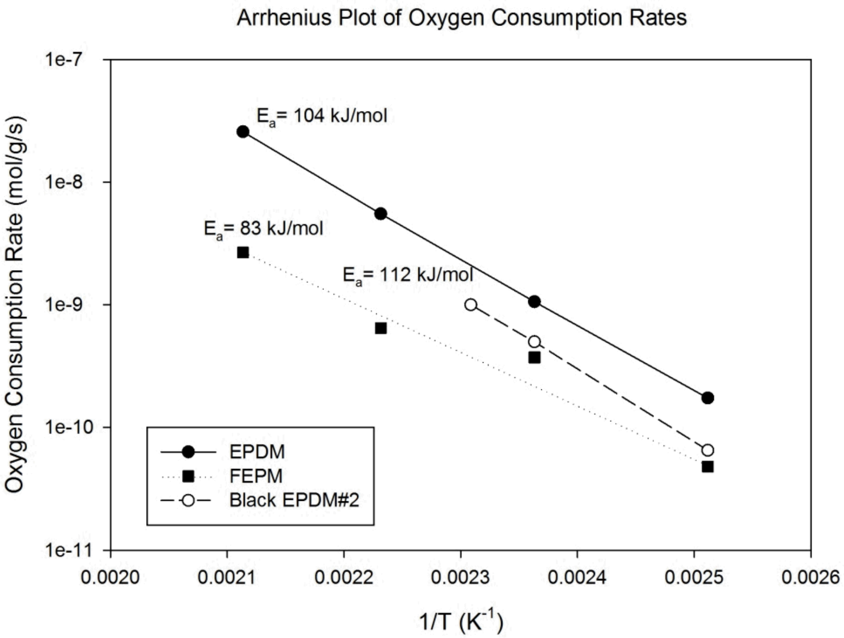
- From these curves, at 300°C:
  - EPDM rate should be ~7e-6 mol/g/s
  - FEPM rate ~ 7e-7 mol/g/s
- Assume O_2 permeability:
  - EPDM ~1e-7 ccSTP/cm/s/cmHg
  - FEPM ~ 5e-7 ccSTP/cm/s/cmHg
- L_{c90}=
  - 0.04 mm EPDM
  - 0.3 mm FEPM

$$L_{c90} = \sqrt{\frac{2 * p * P_{O2}}{\varphi_{Ox} * 22400 * \rho}}$$

$$p = 13.2\ cm\ Hg\ (ABQ, NM)$$
$$\rho = 1\ g/cc$$

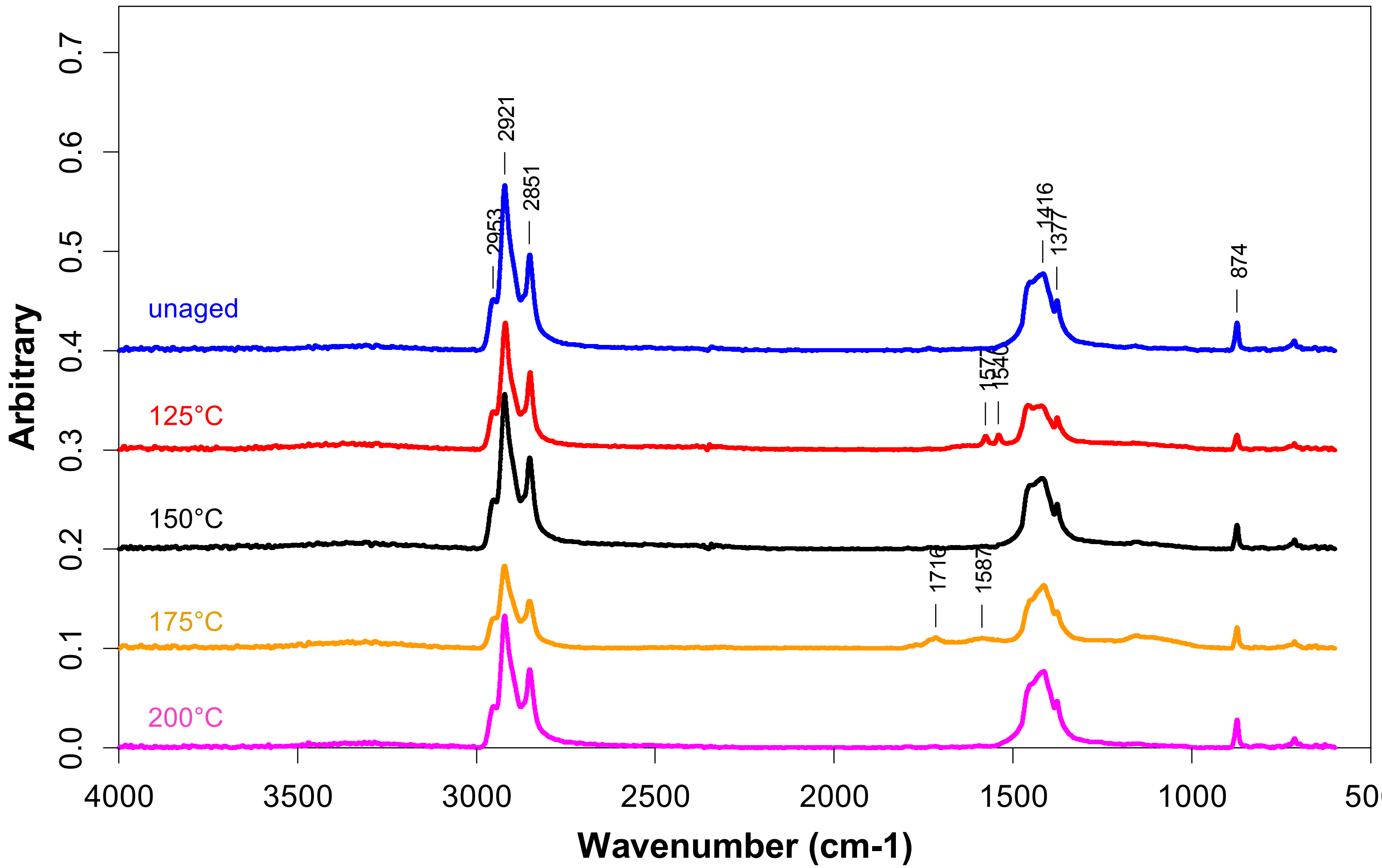
EPDM after thermal cycle

FEPM after thermal cycle



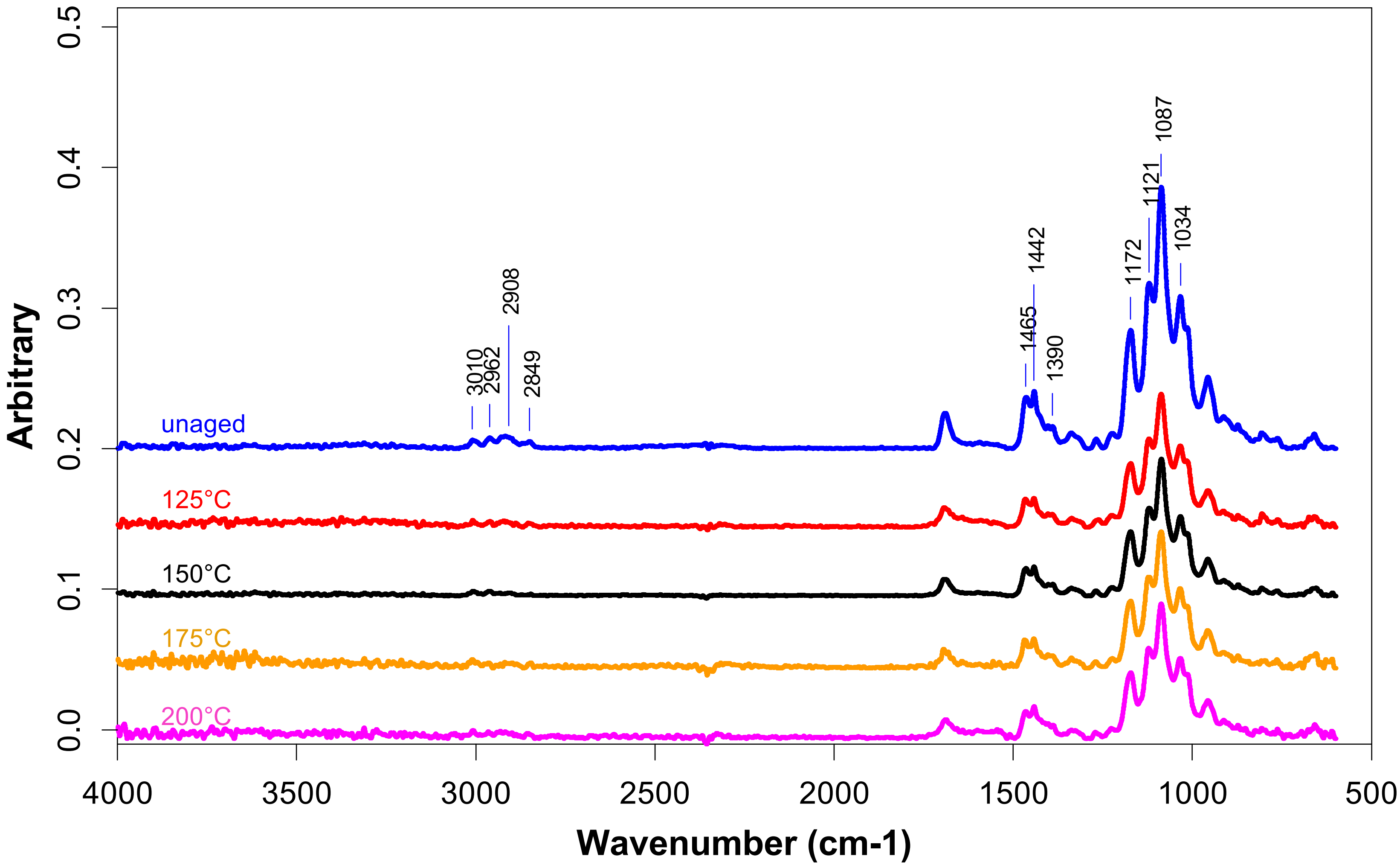
Pieces of the Puzzle – FTIR EPDM Post Ox-Rate

- Appearance of carboxylate species (1540 – 1590 cm^{-1}) and carbonyl (1716 cm^{-1}) after 125 – 175°C oxidation experiments.
- Oxidation byproducts may be released as CO_2 at 200°C (no IR signal).



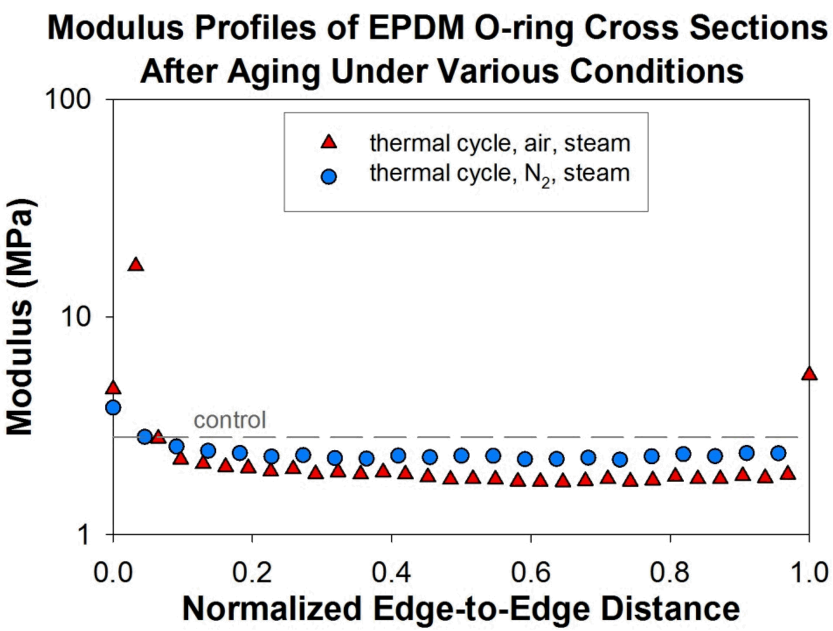
Pieces of the Puzzle – FTIR FEPM Post Ox-Rate

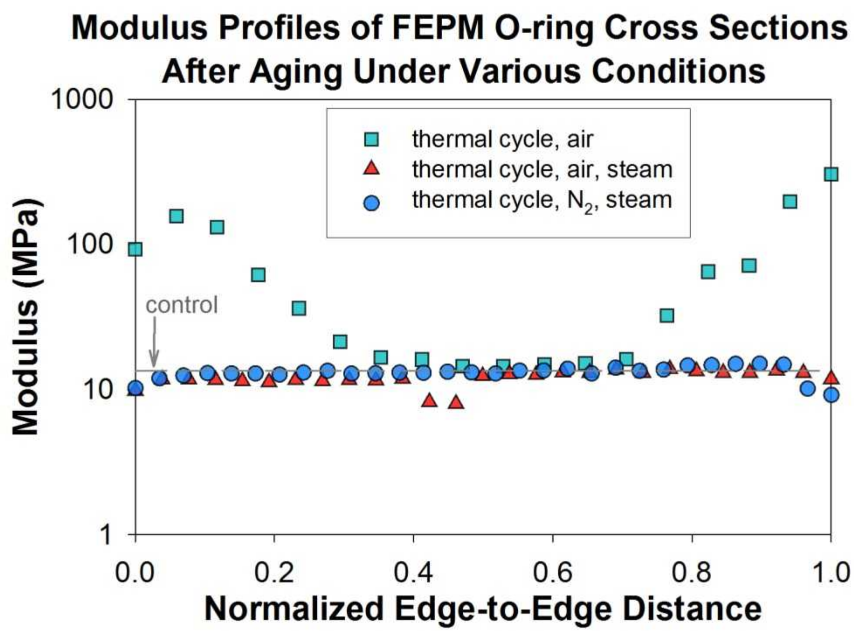
- Reduction in peaks associated with C-H vibrations (2800 cm^{-1} to 3000 cm^{-1}).
  - Indicates degradation occurring through hydrocarbons of propylene segments



Pieces of the Puzzle – Modulus Profiles

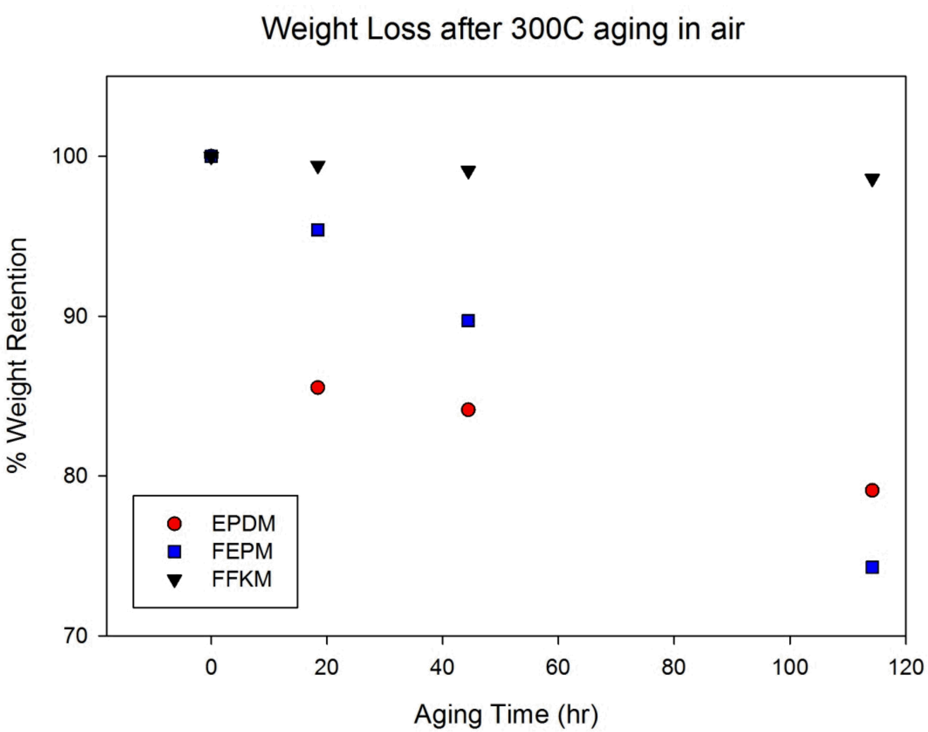
- Edge hardening of EPDM under thermal cycling in air and steam.
- FEPM showed large amounts of edge hardening in thermal cycle/air conditions and small amounts of edge softening in the presence of steam.





Pieces of the Puzzle – Solvent Uptake and Gel Content

- Materials were aged in air at 300°C for 114 hours. Samples were taken periodically and weighed to determine mass loss.
- At the end of aging, elastomers were refluxed in p-xylene for 20 hrs to determine solvent uptake (swelled mass/initial mass) and gel content (final, dried mass/initial mass).



Pieces of the Puzzle – Solvent Uptake and Gel Content

- Materials were aged in air at 300°C for 114 hours. Samples were taken periodically and weighed to determine mass loss.
- At the end of aging, elastomers were refluxed in p-xylene for 20 hrs to determine solvent uptake (swelled mass/initial mass) and gel content (final, dried mass/initial mass).
- Both EPDM & FEPM decrease solvent uptake after aging → indicates crosslinking.
  - Increase in % gel content verifies this for FEPM.
  - Gel content decreased with aged EPDM, but could be due to sample loss from material disintegrating.

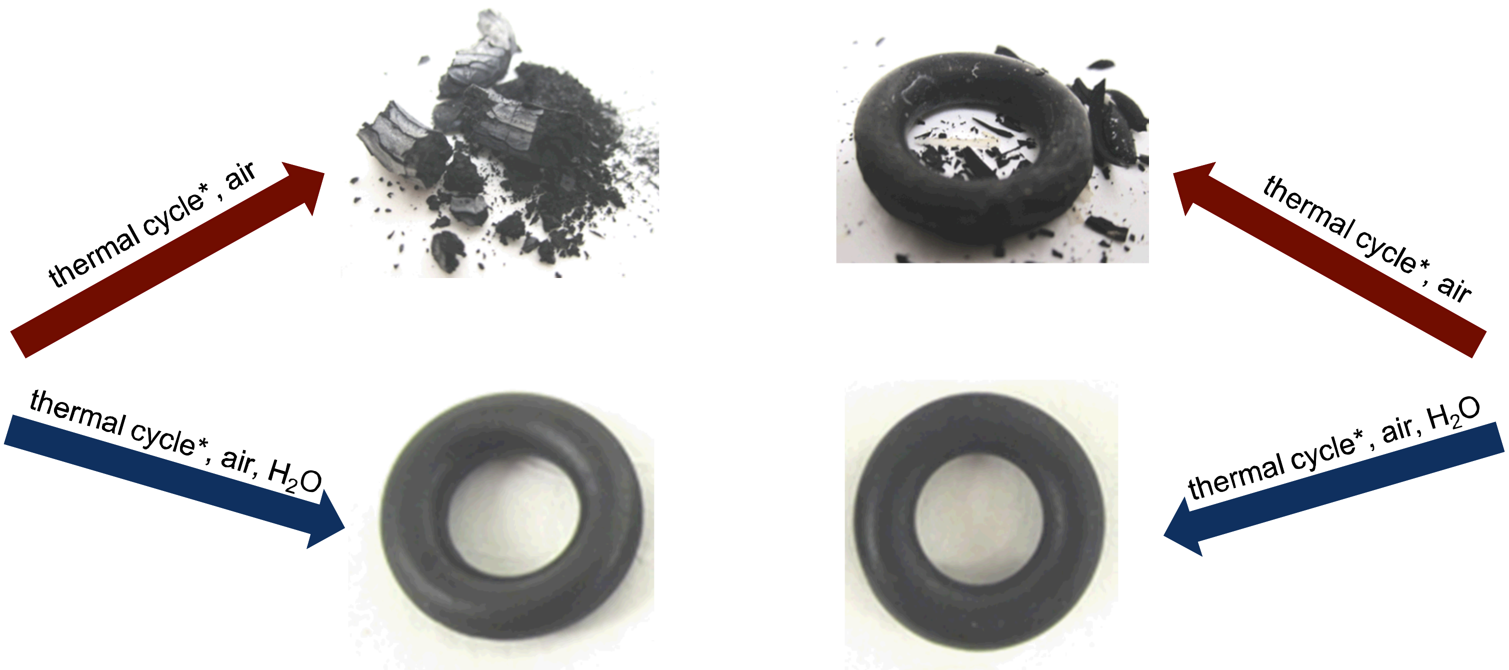
	Uptake Factor	% Gel Content
Unaged EPDM	2.42	88.6
Aged EPDM (300°C, 114 hr)	1.18	79.8*

	Uptake Factor	% Gel Content
Unaged FEPM	1.50	97.0
Aged FEPM (300°C, 114 hr)	1.41	97.4

*Issues with material loss

Putting it all Together

- Based on these results, we *speculate* the unexpected behavior is the result of competition between degradation mechanisms:
  - Thermo-oxidative reactions create crosslinks
  - Thermo-hydrolytic reactions cause chain scission
- Thus, aging at elevated temperatures in the presence of steam leads to improved performance because the scission reactions counteract damage from crosslinking!



Acknowledgements

Sandia National Laboratories

- **Doug Blankenship**
- Douglas Brunson
- **Mat Celina**
- David Chavira
- Greg Cieslewski
- Nicholas Giron
- Charles Harris

Questions??

Drilling Fluid and Brine Chemistries

Sandia National Laboratories

Composition of the simulated drilling fluid	
Major Component	Percent
Water	74 – 83
Barite	10 – 15
Bentonite	5 – 7
Caustic soda	0.3
Soda ash	1
Polyanionic cellulose	0.3 – 1.2
Xanthan gum	0.3 – 0.5
Starch	0.5 – 1

Table 3. Composition of the simulated geo-brine fluid		
Major Components	Compounds	Percent
Cl^-	NaCl	13.5
Na^+	NaCl	6
Ca^{2+}	$CaCl_2$	2
K^+	KCl	1.5
Mg^{2+}	$MgCl_2$	0.9
Minor Components	Compounds	PPM
CO_2	$NaHCO_3$	15,000
Fe^{2+}	$FeCl_2$	1000
Mn^{2+}	$MnCl_2$	930
Li^+	LiCl	410
Zn^{2+}	$ZnCl_2$	370
B^{3+}	H_3BO_3	330
Si^{4+}	Na_2SiO_3	250
Ba^{2+}	$BaCl_2$	130
H_2S	H_2SO_4	70