Hydrogen Fueling Infrastructure Research and Station Technology

# Dispenser Reliability R&D: Materials Compatibility

Annual Merit Review 2019

Crystal City, VA

Michael Peters[1], Nalini Menon[2], Ethan Hecht[2], Tiffany Longfield[2], April Nissen[2], Jeff Campbell[2]

## Project ID: in013

1 – National Renewable Energy Laboratory

2 – Sandia National Laboratory SAND2019-3851C

# Hydrogen First: Program highlights

- NREL and Sandia, CA collaboration started in October'16
- Dispensers are the top causes of maintenance events and downtime at retail H2 stations
- Project focuses on assessing reliability and prediction of lifetimes of fueling and dispensing components exposed to pre-cooled hydrogen at high pressures based on component testing and material analyses

## NREL Role

- Plan, build test set-up and conduct Highly Accelerated Lifetime Testing (HALT) of $H_2$ components
- Survival analysis to determine probability of failure of components and determine failure modes

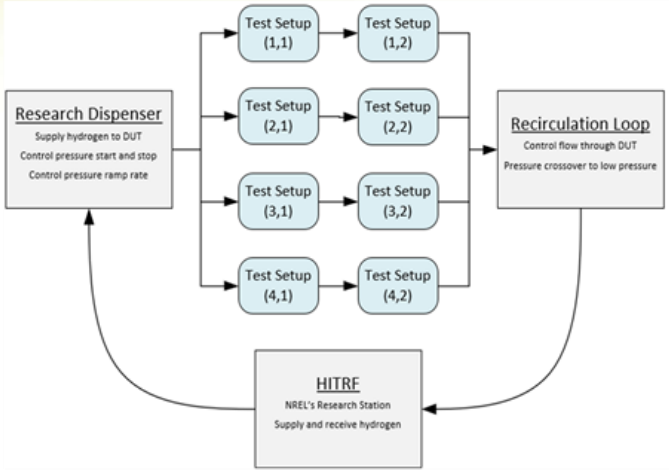
## SNL Role

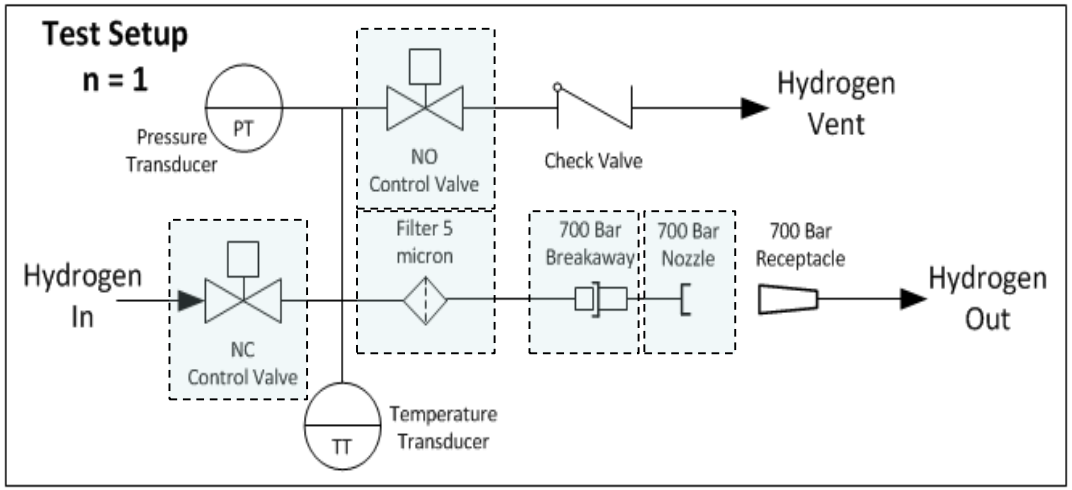
- **Support NREL's project goal of dispenser lifetime prediction with post-exposure compatibility analyses of polymeric materials in failed, and non-failed fueling and dispenser components**

# Approach: Accelerated Reliability Testing

- Measure mean fills between failures (MFBF) and mean kilograms between failures (MKBF) of hydrogen components subjected to pressures, ramp rates, and flow rates similar to light duty fuel cell electric vehicle fueling at -40°C, -20°C, and 0°C
- Devices under Test (DUTs) include nozzles, breakaways, normally closed valve, normally open valve, and filters
- Total of 10 components tested from multiple suppliers for each DUT
- Highly Accelerated Life Test (HALT) of multiple dispenser-like systems simultaneously
- Survival analysis to determine probability of failure of components and determine failure modes
- **Material analysis of actual tested components to establish causes of failure modes observed and predict component lifetimes**

# Devices under Test (DUTs)




| Component | Supplier A | Supplier B |
|---|---|---|
| Breakaways | Walther Prazision | WEH |
| Fueling nozzles | Walther Prazision | WEH |
| Normally open valves | Parker | HiP |
| Normally closed valves | Parker | HiP |
| Filters | Maximator | Autoclave Engineers |

**Multiple suppliers of components points to possibility of different polymeric materials in the same component type**

# Testing factors and response variables

Leverage the National Fuel Cell Technology Evaluation Center (NFCTEC)'s station and vehicle data to define an average fill at a retail station

| Fixed Factors |
|---|
| **Controlled** |
| H2 pressure ramp rate (> 17.6 MPa/min) |
| H2 flow rate (0.8 kg/min) |
| H2 pressure range (14.7-77.9 MPa) |

| Variable Factors | | | |
|---|---|---|---|
| **Controlled** | | **Uncontrolled** | |
| H2 temperature | -40, -20, 0C | Ambient temperature | 10 - 40C |
| Component types | Nozzles<br>Breakaways<br>NO valves<br>NC valves<br>Filters | Ambient humidity | 0 - 100% |

| Response Variables | |
|---|---|
| **H2 leak (qualitative)** | **Yes or No** |
| **Fills before failure (quantitative)** | **Number** |
| **Amount of H2 through component before failure (quantitative)** | **Kilograms** |

**Important to know polymer exposure environment**

# Polymers for hydrogen environments

- Polymers are used extensively in the hydrogen infrastructure for :
  - ❑ Distribution and Delivery (Piping and Pipelines)
  - ❑ Fueling Stations
  - ❑ Vehicle Fuel Systems

- Component designs such as tanks, pipeline liners, valves, O rings, gaskets, regulators, pistons and other fittings are made of polymers
- Conditions of high pressures (0.1 to 100 MPa) and rapid cycling of temperatures (-40˚C to +85˚C) possible during service

**Elastomers**
**EPDM, NBR/HNBR Levapren, Silicone, Viton, Neoprene**

**Thermoplastics**
**HDPE, Polybutene, Nylon, PEEK, PEKK, PET, PEI, PVDF, Teflon, PCTFE, POM**

**Thermosetting polymers**
**Epoxy, PI, NBR, Polyurethane**

# Typical polymer characterization techniques

- **Microscopy (ND)**
  - Optical (Keyence) – blisters, external cracks, surface roughness/texturing, damage in the form of bubbles and/or tears or shredding
  - Micro Computed Tomography – internal cracks and voids
  - Permanent damage
- **Density (ND)**
  - ASTM B962-17 – specific volume changes or swelling due to uptake of H2
  - Can be permanent or transient (comes back to original density)
- **Hardness (ND)**
  - Shore A hardness changes for permanent change in microstructure by crosslinking or scission
  - Nano indentation for coefficient of friction changes due to H2 exposure on surface
- **Compression Set (D)**
  - ASTM 395 – permanent deformation that indicates crosslinking or permanent microstructural changes
  - Applicable to elastomers only
- **Mechanical Strength (D)**
  - Changes in Young's Modulus, tensile strength, tear strength from microstructural changes

**ND** = Non-destructive; can be used for multiple characterization tests; **D** = Destructive; specimen not reusable

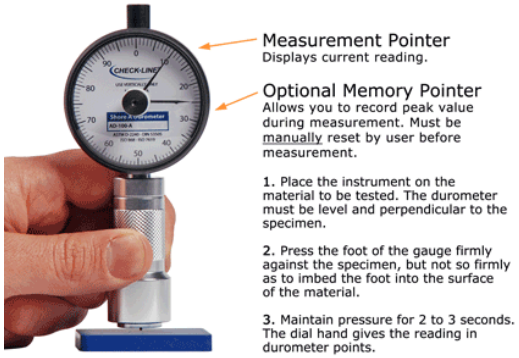
# More polymer characterization techniques

- **Chemical characterization (all ND) except DMTA (D)**
  - Fourier-transform infra Red (FTIR) spectroscopy – polymer microstructure changes through functionalities identification
  - Raman spectroscopy – changes in intramolecular bonds
  - X-ray diffraction analysis (XRD) – For changes in crystalline domains in elastomers or degree of crystallinity in thermoplastics
  - Nuclear magnetic resonance (NMR) – Structural changes
  - Dynamic mechanical and thermal analysis (DMTA) – $T_g$ glass transition temperature changes and modulus changes
  - Thermal desorption spectroscopy (TDS) – gas capture and release characteristics

**These methods capture permanent structural changes in the polymer**

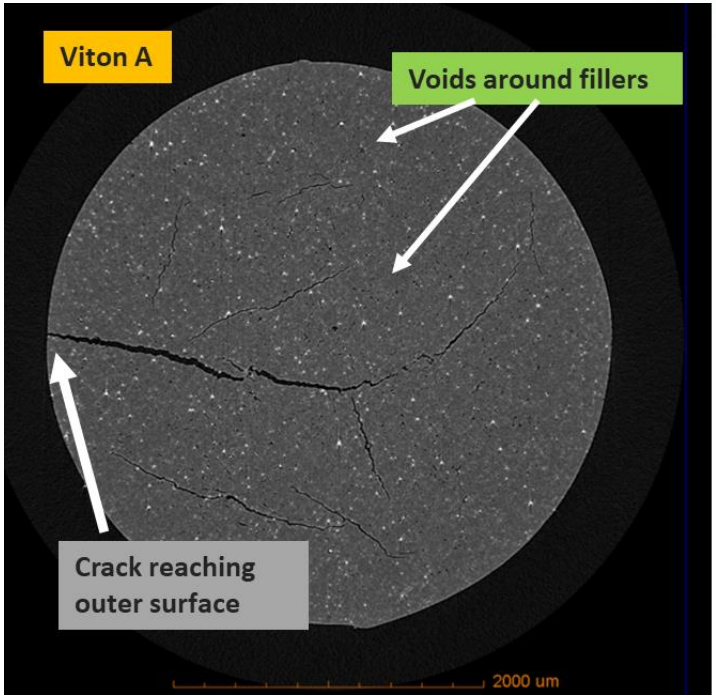
# Some typical polymer characterization outputs

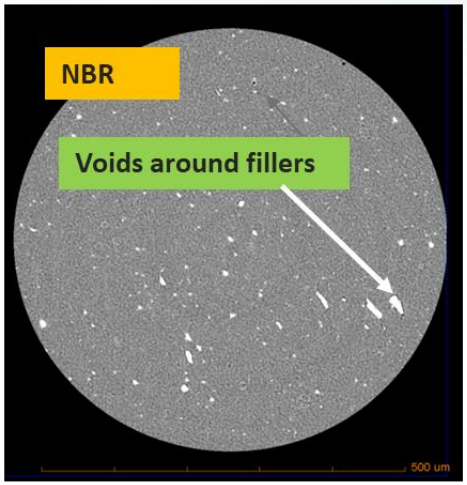
Keyence images of polymer O rings damaged in service




Shore A hardness tester

Micro CT images for cracks originating from the inside



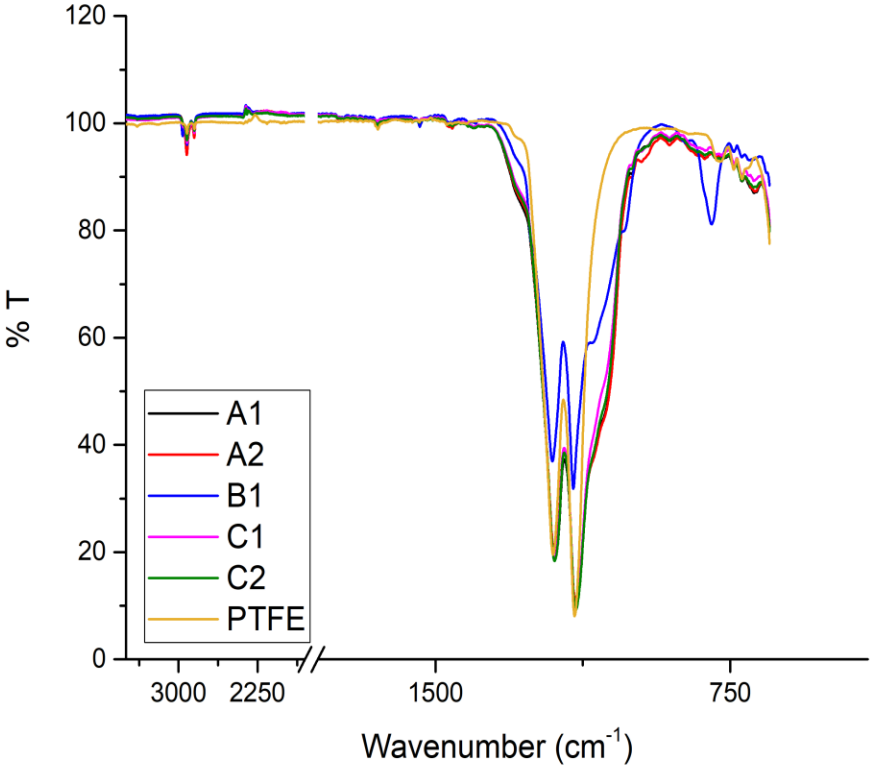




NBR and EPDM shown at 500 microns to magnify any voids or cracks

Change in Coefficient of friction in response to H2 exposure (Nano indentation)

| EPDM | Avg. Friction | Std. Dev Friction |
|---|---|---|
| Before H2 | 0.41 | 0.091 |
| After H2 cyclic | 0.49 | 0.094 |
| After H2 static | 0.63 | 0.095 |

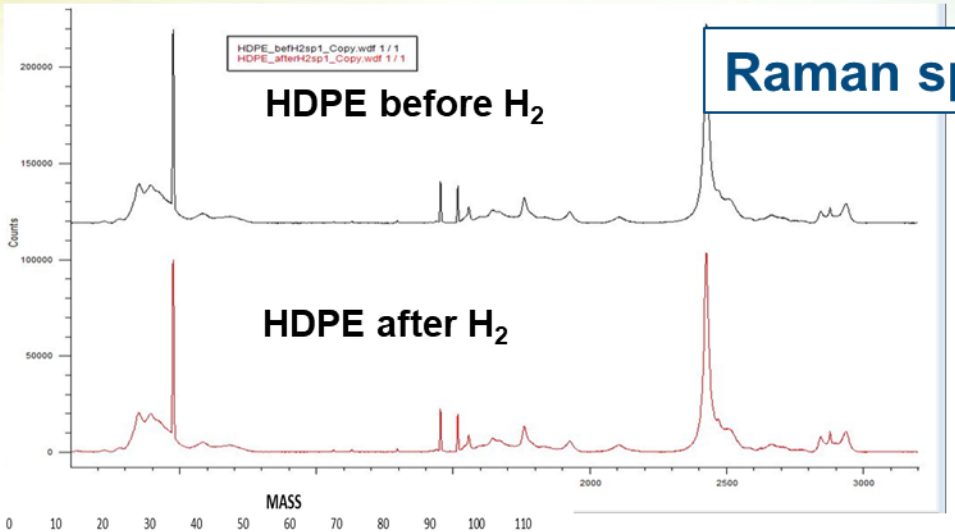
# IR spectroscopy confirming polymer structure



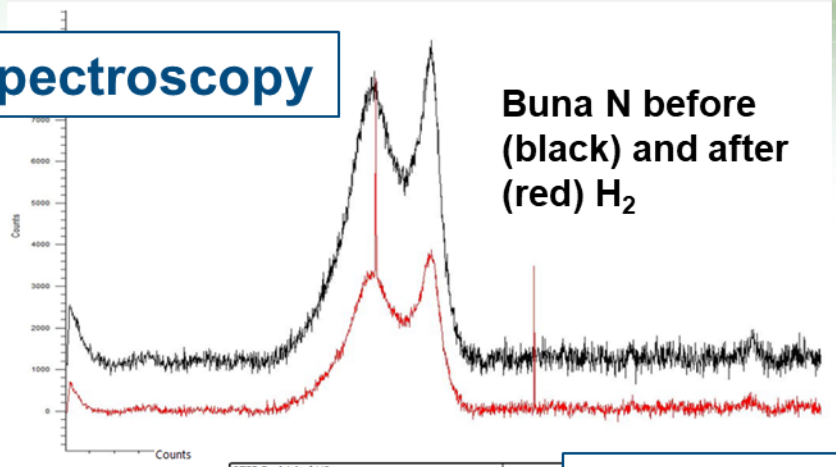

- Material characterization through Infra-red spectroscopy ATR (attenuated total reflectance)
- Easy to use and quick accurate identification possible due to fingerprint region (1500 to 500 $cm^{-1}$); complex bending, rotational and vibrational modes of molecules which are unique to materials
- However, materials such as plastics and elastomers not easy to decipher because they have multiple additives

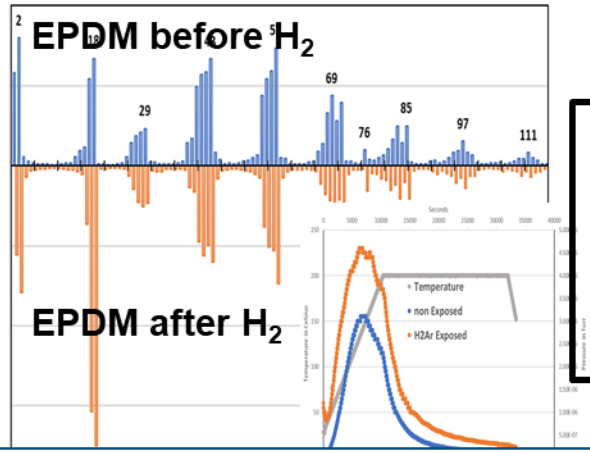
In the figure shown, O-ring B1 (blue) compares well to a standard spectrum of PTFE

# Examples of spectroscopy for structural changes in polymers after H2 exposure



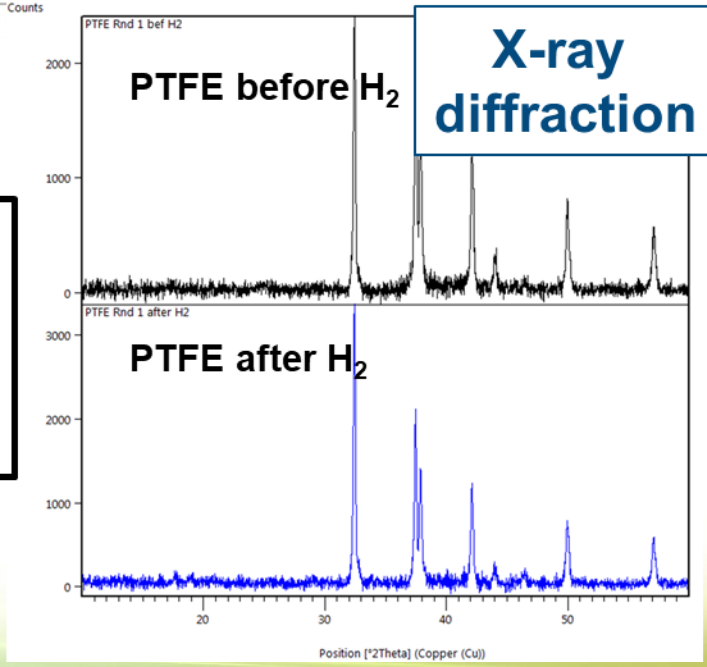

**Raman spectroscopy**



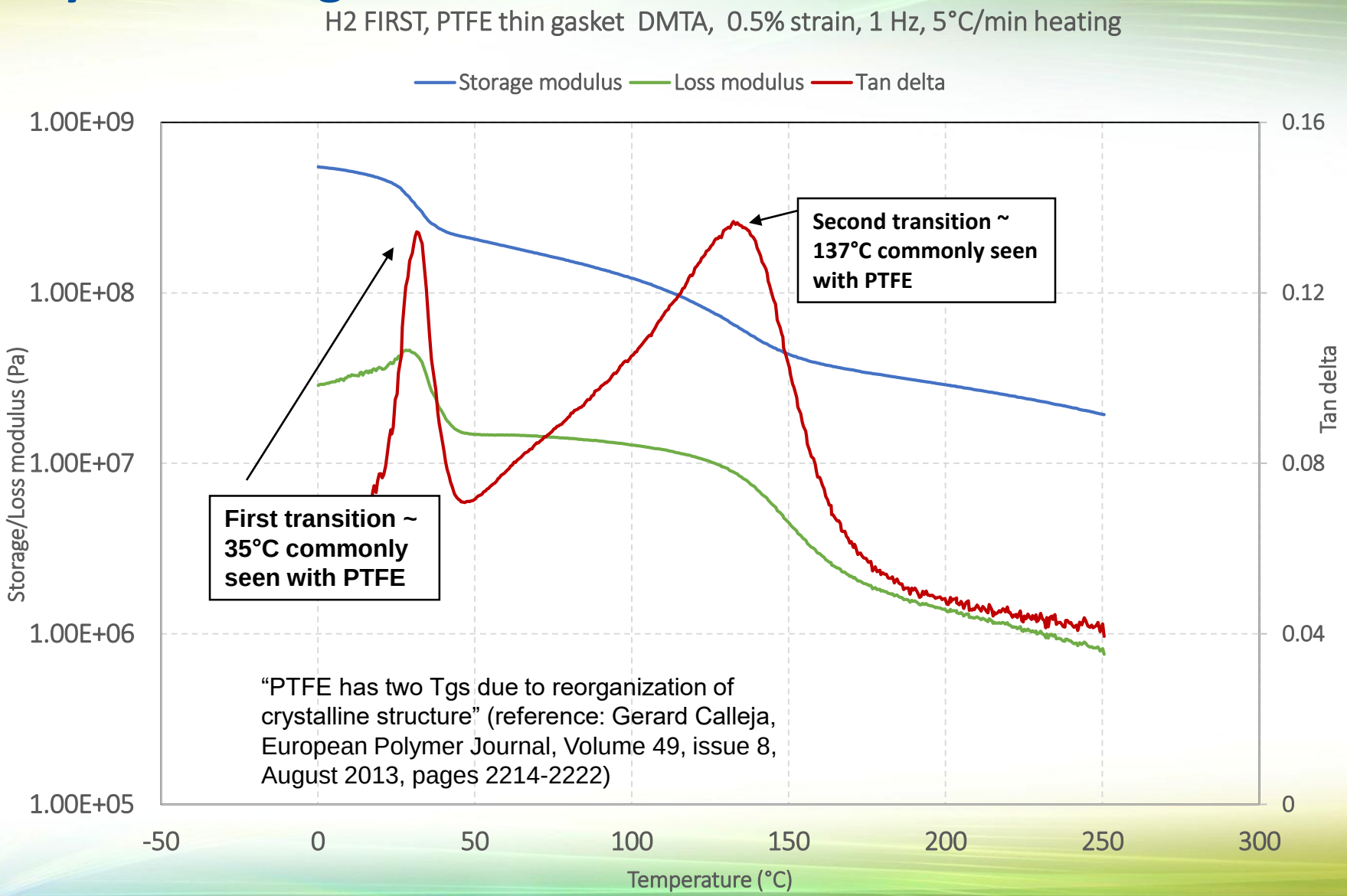

**Suggestion of additional volatility after Ar/H2 exposure**

**Thermal desorption spectroscopy**



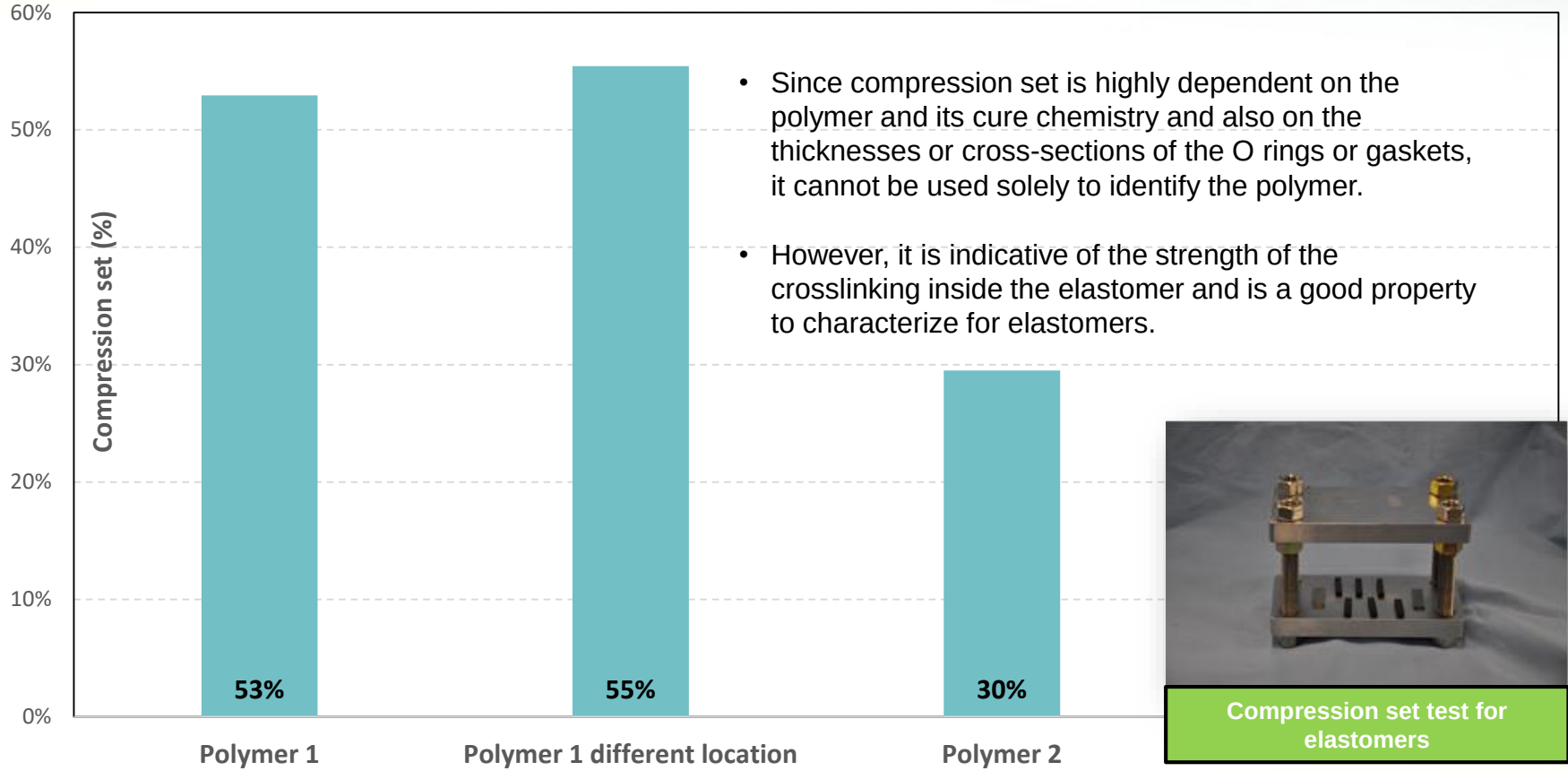

**X-ray diffraction**

# Example of chemical identification of polymers using DMTA



# Example of compression set property of elastomers

**Compression set of elastomeric O rings from H2 FIRST parts**
**Under 25% compression at 110°C for 22 hours, recover 30 minutes (ASTM D 395 Method B)**




- Since compression set is highly dependent on the polymer and its cure chemistry and also on the thicknesses or cross-sections of the O rings or gaskets, it cannot be used solely to identify the polymer.
- However, it is indicative of the strength of the crosslinking inside the elastomer and is a good property to characterize for elastomers.



Compression set test for elastomers

# Materials compatibility testing steps

**Component Testing**

Multiple components at the same time – 1000 cycles at each temp.

Failed and non-failed components

Survival analysis

**Unexposed Components**

Characterization of polymers retrieved for chemical identity

Database of baseline properties for unexposed polymers

**Exposed components**

Characterization of exposed polymers

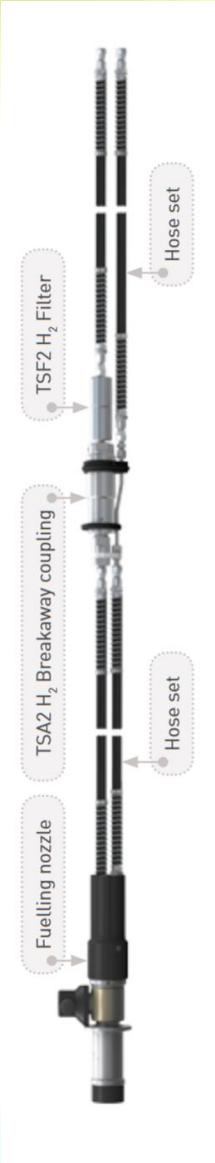
Compare to unexposed polymer properties for failure modes, technical basis for the same

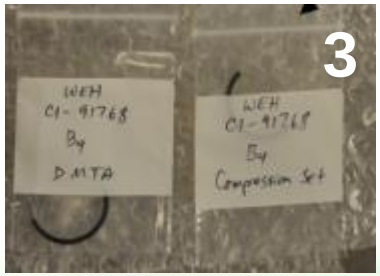
# NREL components received for Material Analyses

| Component | Manufacturer (ID protected) | NREL ID | SNL ID | Tested or not tested |
|---|---|---|---|---|
| Breakaways | A | BR001 | 1B | Not tested, control |
| | B | BR006 | 2F | Not tested, control |
| | A | BR018 | 3C | Tested and failed |
| | B | BR026 | 2G | Not tested, control |
| Fueling nozzle | A | FN001 | 2B | Not tested, control |
| | B | FN050 | 2D | Not tested, control |
| 2 Way straight valve normally open | C | NO001 | 2A | Not tested, control |
| | D | NO026 | 1E, 1D, 1C, 1A | Not tested, control |
| 2 Way straight valve normally closed | C | NC001 | 2C | Not tested, control |
| | D | NC026 | 1A, 1C, 1D | Not tested, control |
| | D | NC047 | 3D | Tested and failed |
| | D | NC049 | 3A | Tested and failed |
| Filters | E | MF026 | 00, no polymers | Not tested, control |
| | F | MF001 | 2E, no polymers | Not tested, control |
| | E | No marking | 3E, no polymers | Tested, no polymers |

All incoming parts are logged into an internal database for traceability

# Disassembly of components






**Same sequence of steps used to process both exposed and unexposed components**

1. Pictures taken of whole components received from NREL with NREL designation clearly depicted
2. Component disassembled carefully with special tools so as to not alter polymer physical form
3. Polymer O rings retrieved are bagged individually and assigned special combo of letter and number to indicate component source, entered into database
4. Polymer pictures taken and stored along with whole component pictures
5. Specimens distributed to non-destructive testing first followed by destructive testing

# Samples of components received

2 way straight normally closed valve

2 way straight normally open valve

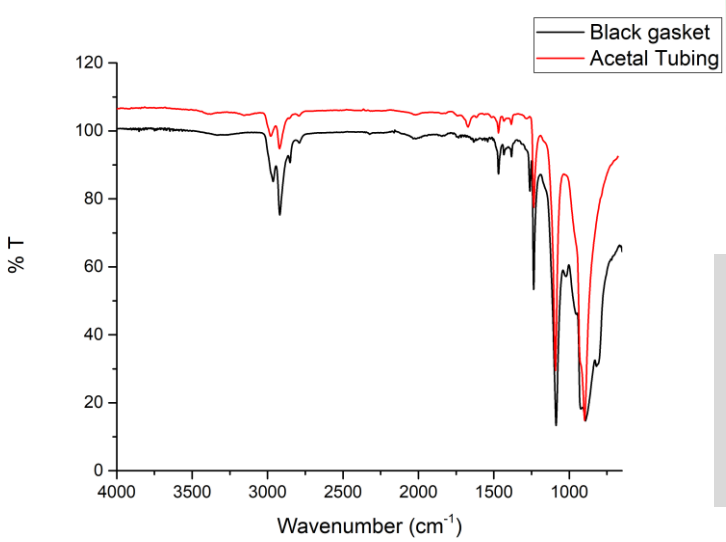
Breakaway devices

Fueling nozzles

Filters

Five different components from six suppliers

# First step: Identify O ring chemistry in components

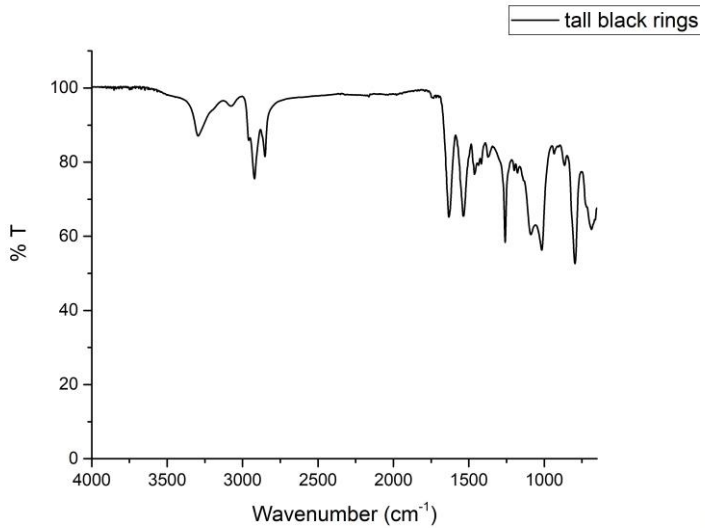



2B1 Black gasket

Acetal

**FT-IR spectra shown for manufacturer A Fueling Nozzle NREL FN001/2B**

**O rings retrieved from this component were analyzed using FTIR and then compared to standard spectra for these compounds**



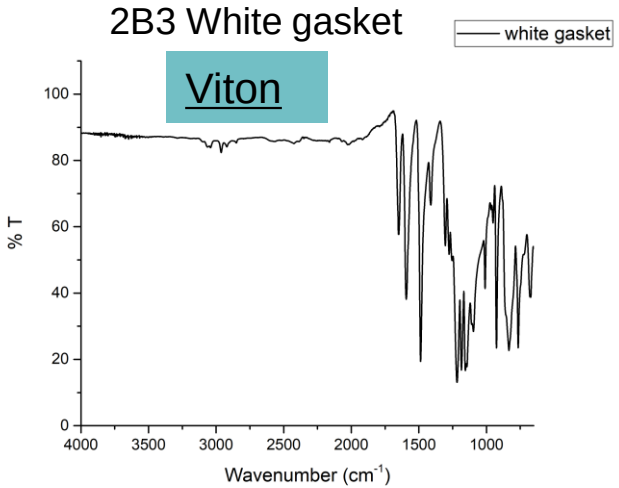

2B2 tall black ring

Nylon

- **N—H bond present at 3295 $cm^{-1}$**
- **Bands corresponding to presence of epoxide group observed**
  - **1259 $cm^{-1}$**
  - **1089 $cm^{-1}$**
  - **1016 $cm^{-1}$**
  - **796 $cm^{-1}$**

2B3 White gasket

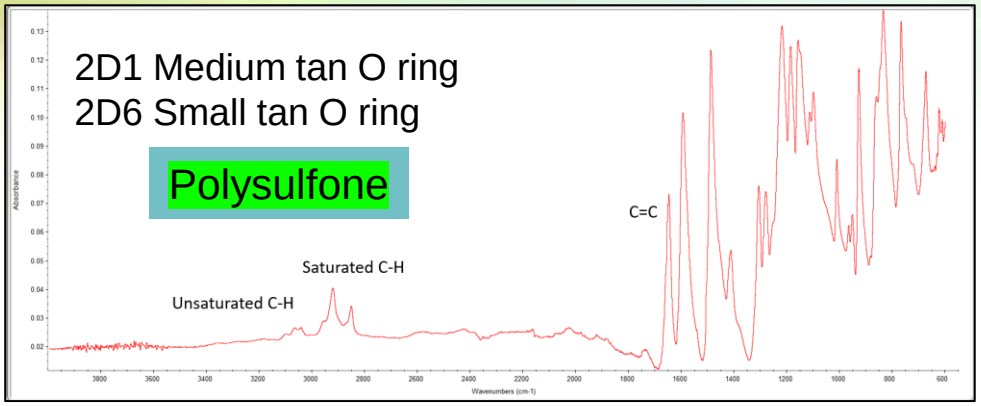
Viton

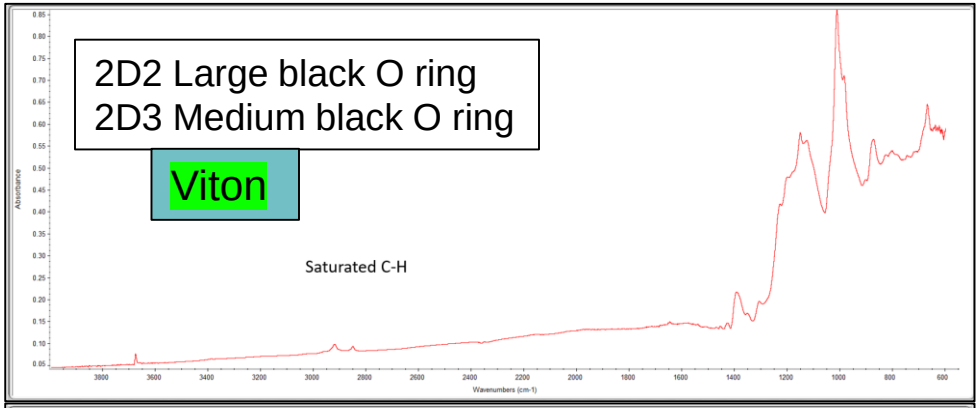


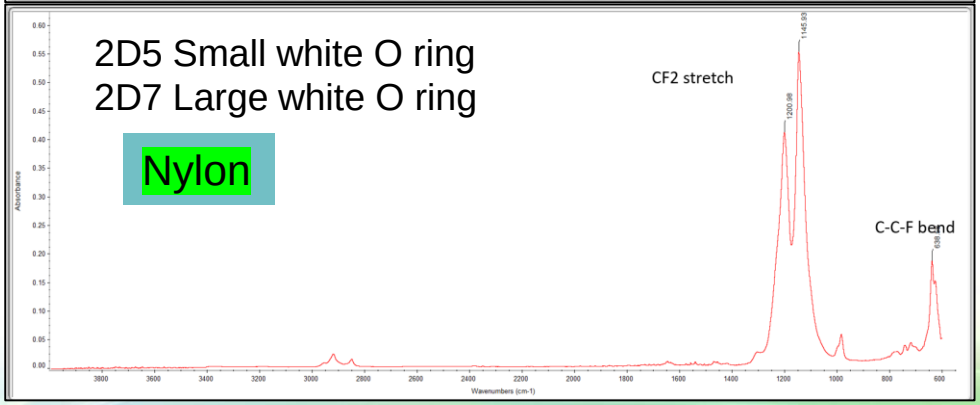

- **Some C—H bands observed above 3000 $cm^{-1}$ indicate unsaturated material**
- **C=C observed at 1651 $cm^{-1}$**
- **Further analysis of bands needed**

**Different manufacturers of components use different polymers (compare to next slide)**

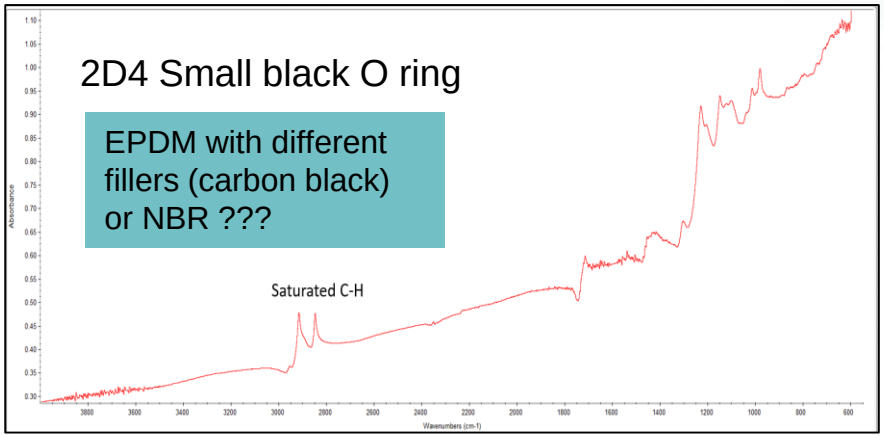
# Comparing O rings in similar components from Manufacturer B



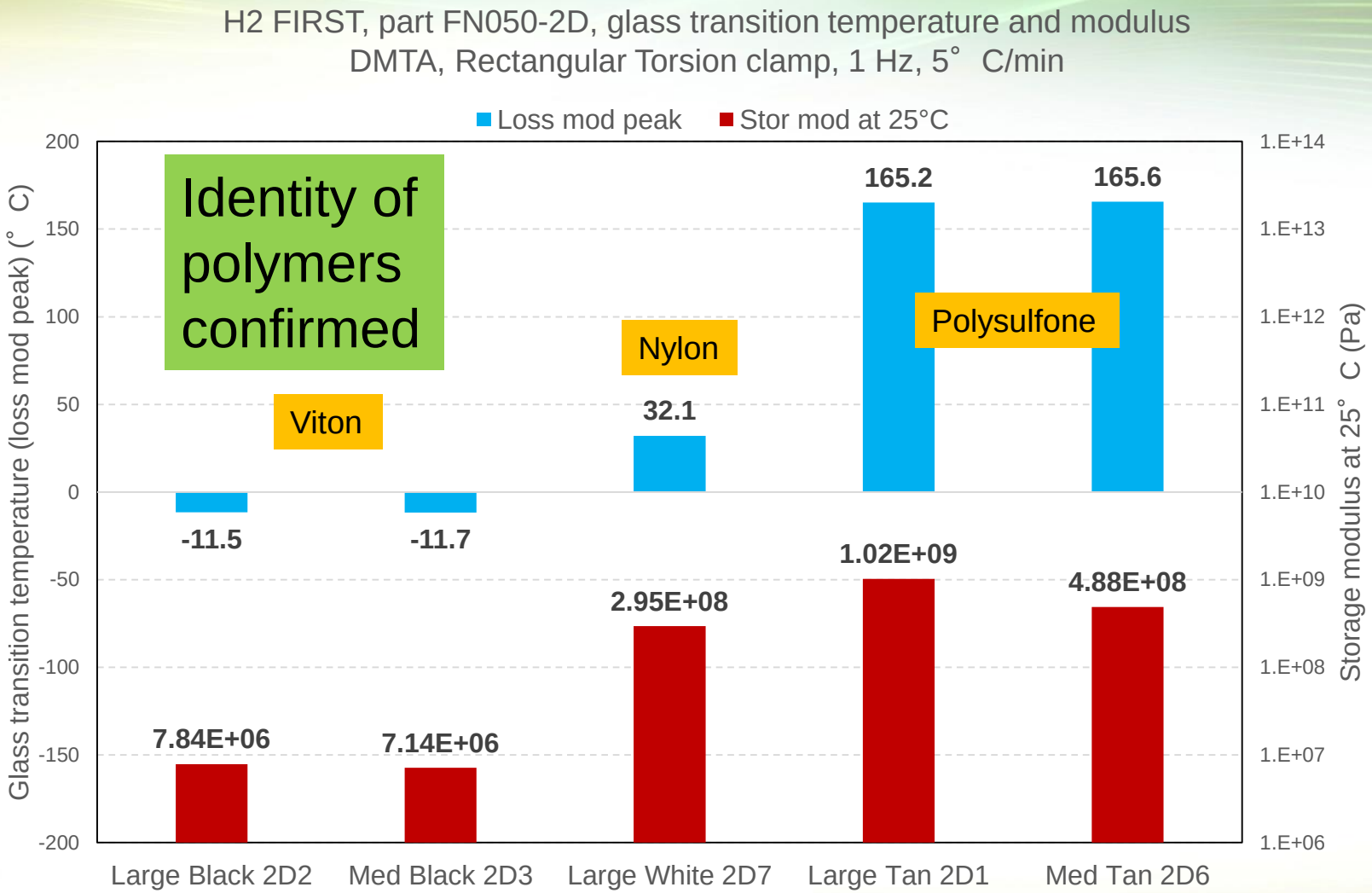




**FT-IR spectra shown for manufacturer B Fueling Nozzle NREL FN050/2D**




- Functionally identical components from different manufacturers can be built with different polymer O rings
- **Multiple analytical methods need to be used to confirm polymer identity (see DMTA data on next slide)**

# DMTA analysis: Fueling Nozzle NREL FN050/2D




**Confirmation of FTIR findings (previous slide) with glass transition temperatures (DMTA)**

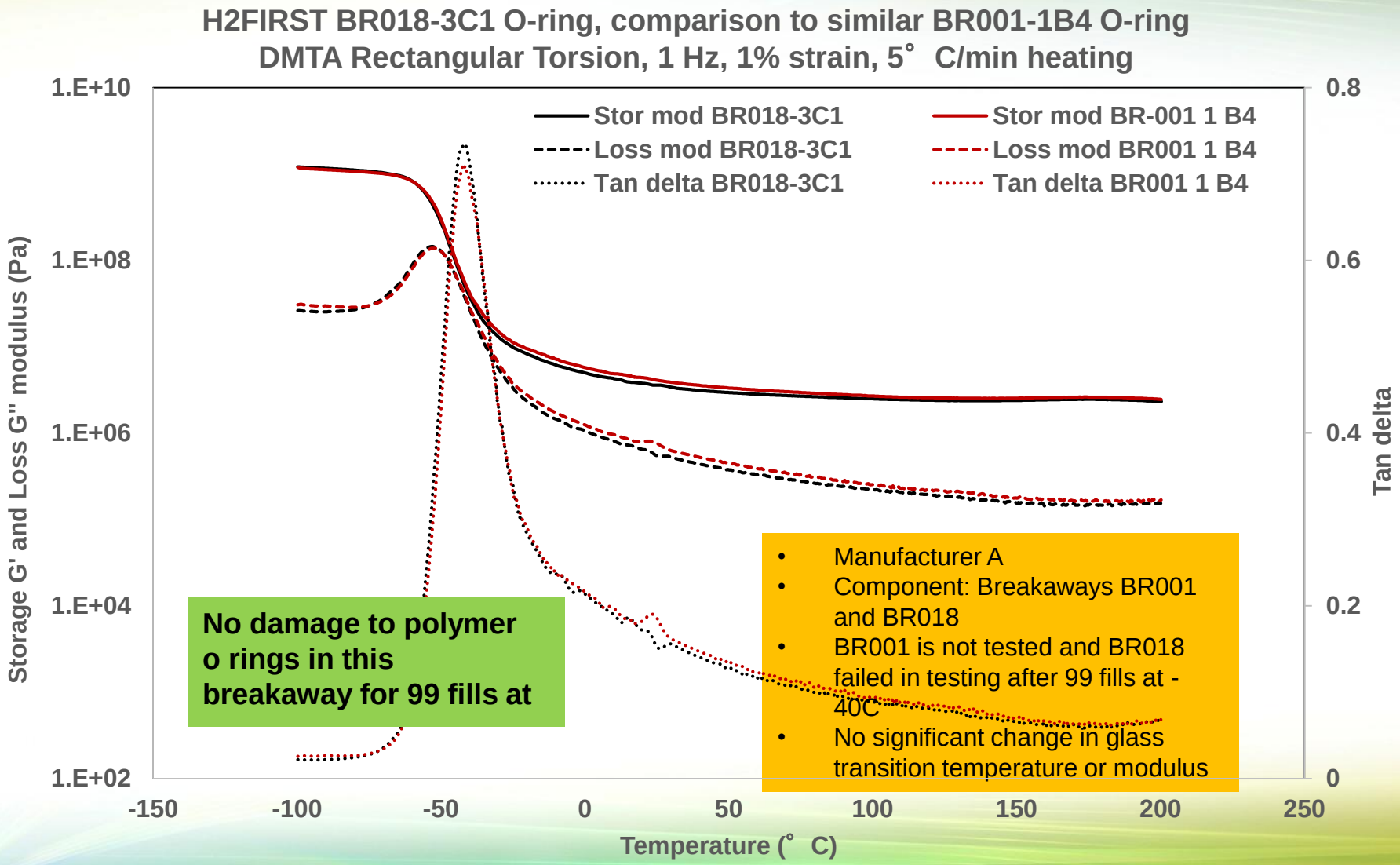
# Failed components received from NREL

The table below shows the failed components and the number of fills they completed before failure at -40C

| Part Description | Manufacturer | Part Identifier (sticker) | Number of Fills | Fill Temp Target (C) |
|---|---|---|---|---|
| **Normally Closed Valve** | D | NC047 | 99 | -40 |
| **Normally Closed Valve** | D | NC049 | 99 | -40 |
| **Breakaway** | A | BR018 | 132 | -40 |
| **Filter** | E | - | - | - |

Next step would be to compare the polymers retrieved from these failed components against unexposed/untested ones.

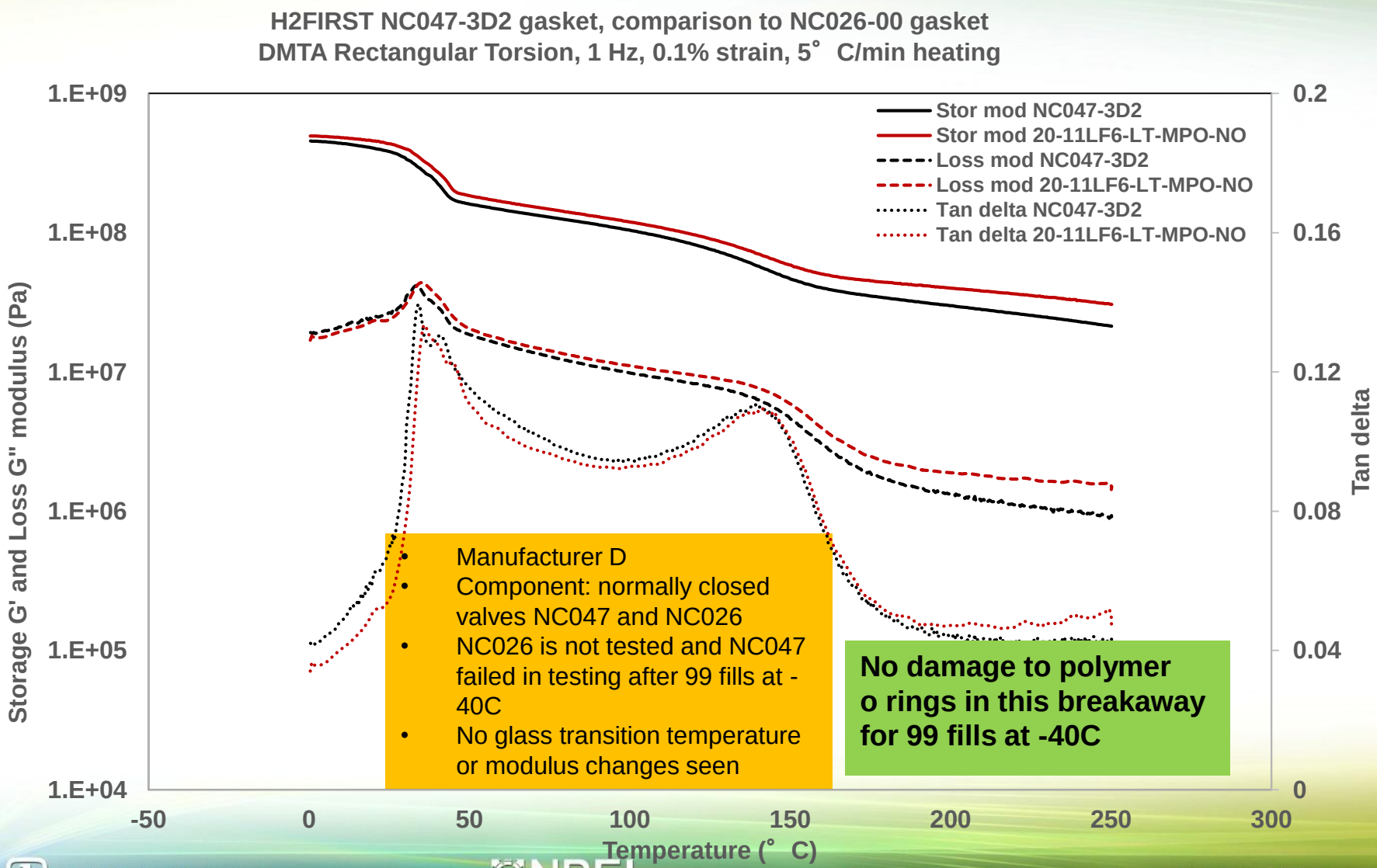
# Comparison of polymers before and after exposure in breakaways (Example 1)




**No damage to polymer o rings in this breakaway for 99 fills at**

- Manufacturer A
- Component: Breakaways BR001 and BR018
- BR001 is not tested and BR018 failed in testing after 99 fills at -40C
- No significant change in glass transition temperature or modulus

# Comparison of polymers before and after exposure in normally closed valves (Example 2)




- Manufacturer D
- Component: normally closed valves NC047 and NC026
- NC026 is not tested and NC047 failed in testing after 99 fills at -40C
- No glass transition temperature or modulus changes seen

**No damage to polymer o rings in this breakaway for 99 fills at -40C**

# Conclusions

- NREL and Sandia collaborated Dispenser Reliability project has completed ~ 1000 cycles of component testing at -40C
- Three significant failures (two normally closed valves and a breakaway) seen so far
- Material analyses used to establish baseline properties of polymer O rings in the components before exposure
- Failure mode analyses through material characterization after exposure can be used for survival analysis and lifetime predictions
- Multiple characterization methods are currently being used in synergy to measure property changes
- Analyses are in progress at this time on the -40C parts
- Support to tests at -20C and 0C to continue

Michael Peters – NREL – Michael.Peters@NREL.gov

Nalini Menon – SNL – ncmenon@sandia.gov

Any Questions?

# THANK YOU

# EXTRA SLIDES

# AFT Models, Factors and Levels of DRP

AFT Models:

- Parametric models frequently used in reliability testing
- Used often especially in expensive experiments
- Fast method to determine probability of failures of components and determine failure mode

Factors of DRP:

- Manufacturer of part
  - At most 2 manufacturers per part
  - 50 units of each of the six different components

Levels of DRP:

- Temperature of Hydrogen
  - 3 different temperatures of hydrogen

Tracking:

- All parts will be tracked by barcode and stored in FileMaker
- No parts will be used on different temperatures
- Failed parts will not be repaired
- Censored parts are subject to continued testing

- Median Rank Method is not as accurate or precise as MLE or Kaplan-Meier
- Median Rank Method is more complicated and requires more transformations
- MLE and Kaplan-Meier are simple
- Results consistently show MLE method is the most accurate and precise
- Kaplan-Meier should be used to determine distribution of failure times
- Distribution found with Kaplan-Meier should be used for MLE method
- MLE and Kaplan-Meier methods are more efficient to run and more versatile than Median Ranks