Hydrogen Fueling Infrastructure Research and Station Technology

Dispenser Reliability R&D: Materials Compatibility

Annual Merit Review 2019

Crystal City, VA

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Project ID: in013

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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

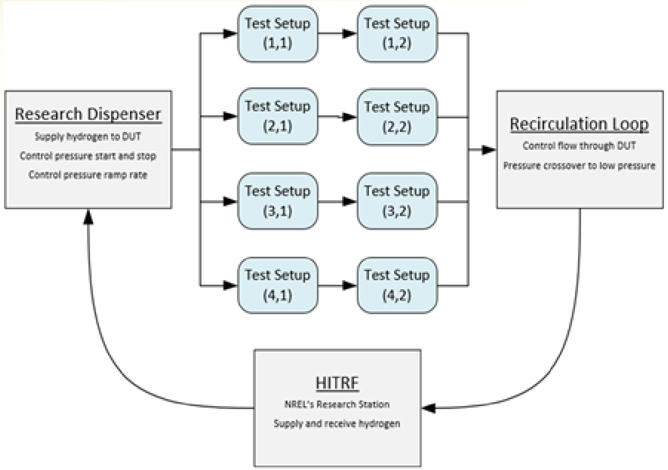
SNL Role

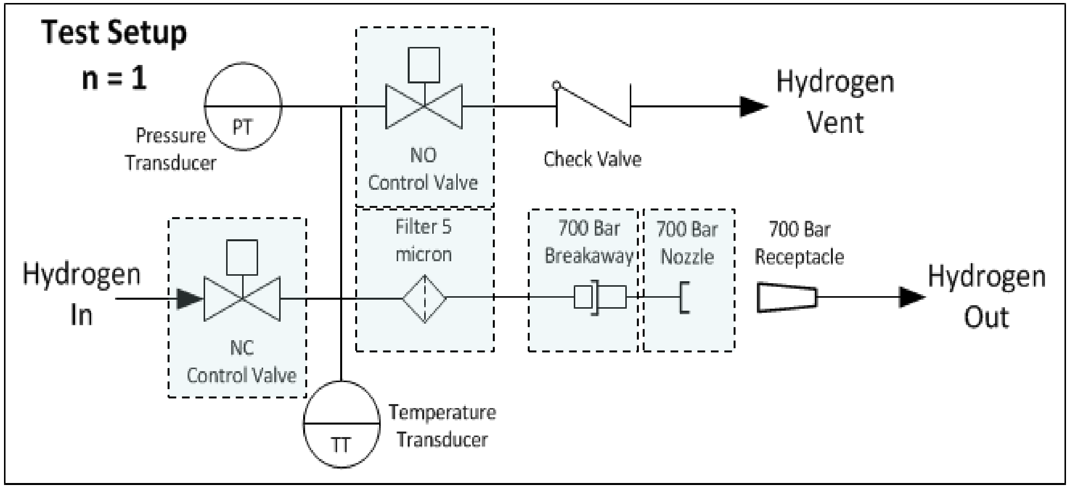
- **Support NREL’s project goal of dispenser lifetime prediction with post-exposure compatibility analyses of polymeric materials in failed, and non-failed fueling and dispenser components**

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^{o}C, -20^{o}C, and 0^{o}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 Breakaways NO valves NC valves 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

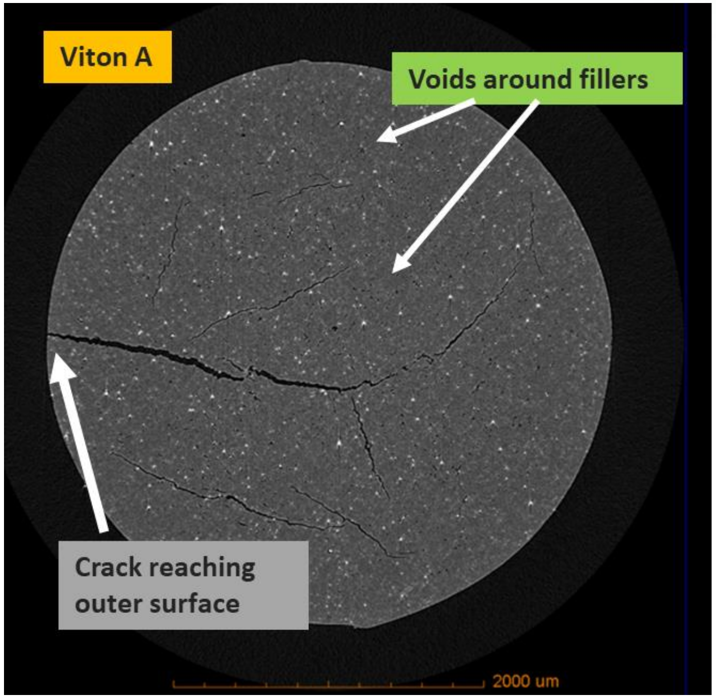
Measurement Pointer
Displays current reading.

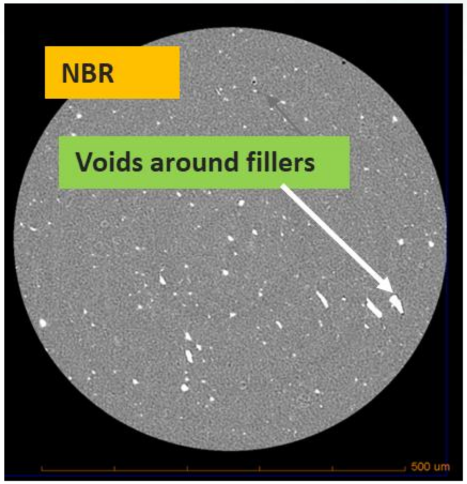
Optional Memory Pointer
Allows you to record peak value during measurement. Must be manually reset by user before measurement.

1. Place the instrument on the material to be tested. The durometer must be level and perpendicular to the specimen.
2. Press the foot of the gauge firmly against the specimen, but not so firmly as to imbed the foot into the surface of the material.
3. Maintain pressure for 2 to 3 seconds. The dial hand gives the reading in durometer points.

Shore A hardness tester

Micro CT images for cracks originating from the inside



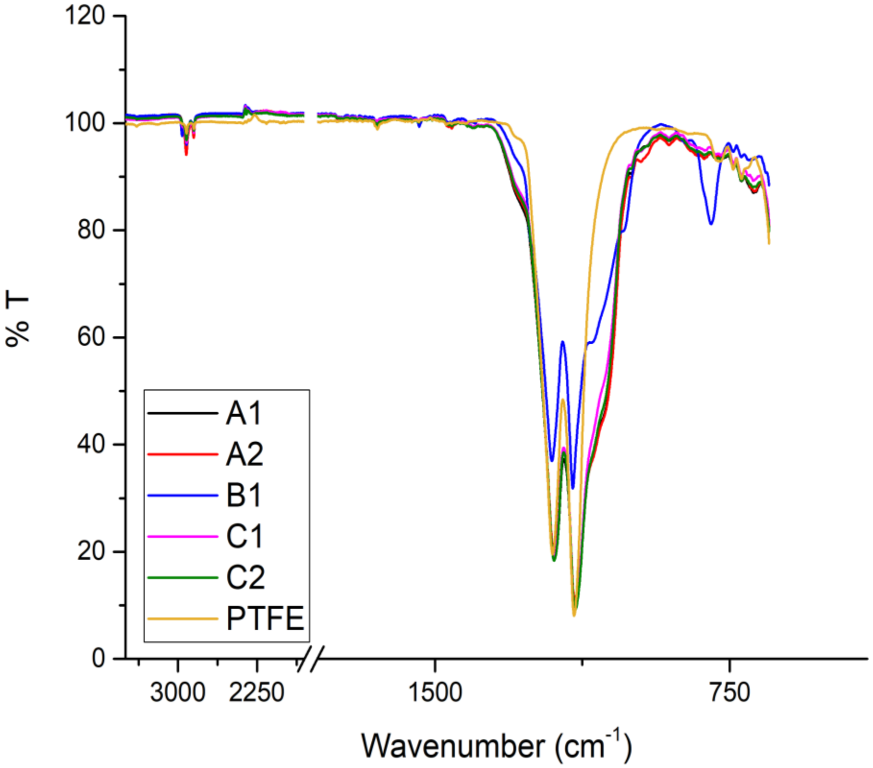


NBR and EPDM shown at 500 microns to magnify any voids or cracks

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

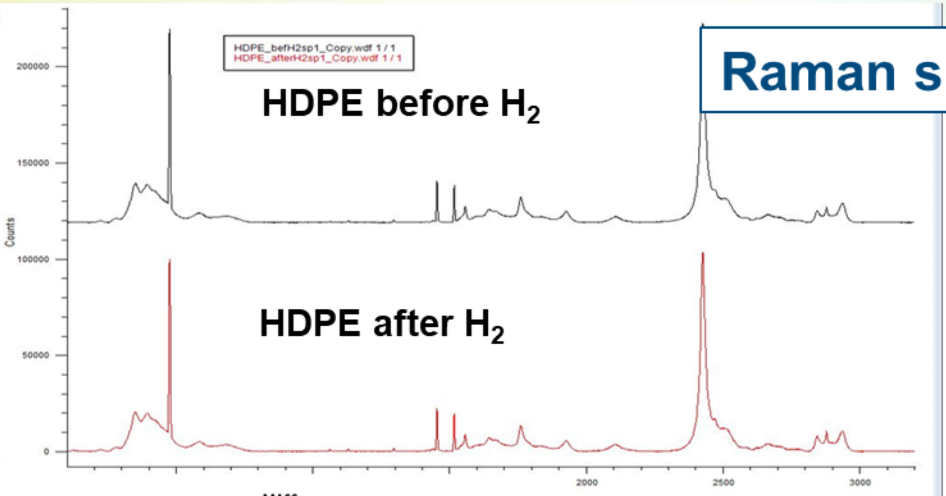


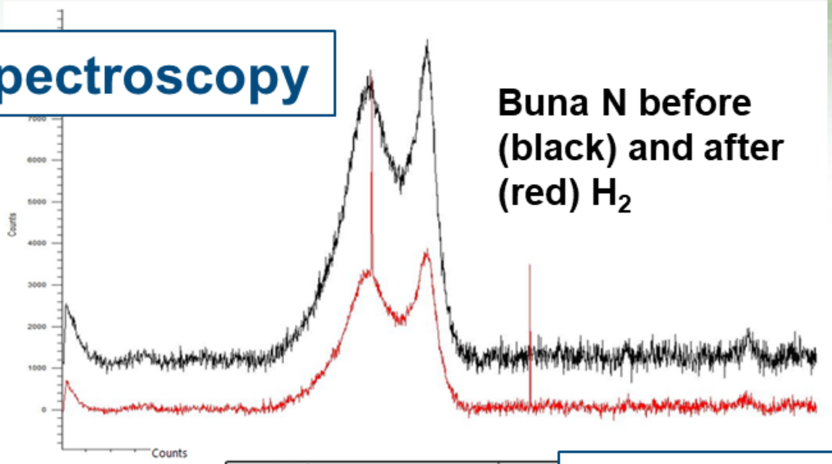
- Material characterization through Infra-red spectroscopy ATR (attenuated total reflectance)
- Easy to use and quick accurate identification possible due to fingerprint region (1500 to 500 cm^{-1}); complex bending, rotational and vibrational modes of molecules which are unique to materials
- However, 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

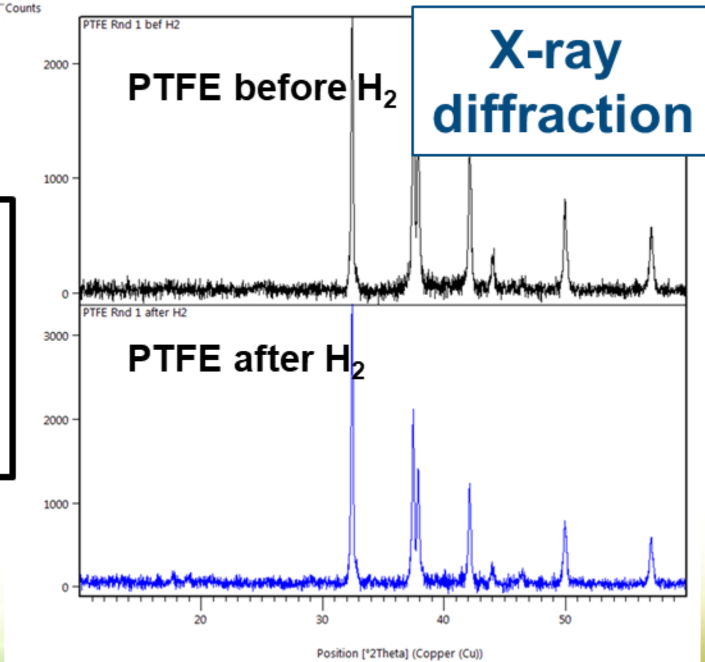
Examples of spectroscopy for structural changes in polymers after H2 exposure

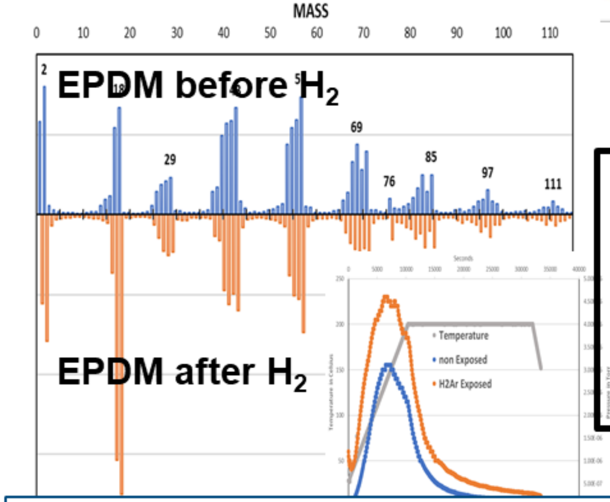
Raman spectroscopy





X-ray diffraction

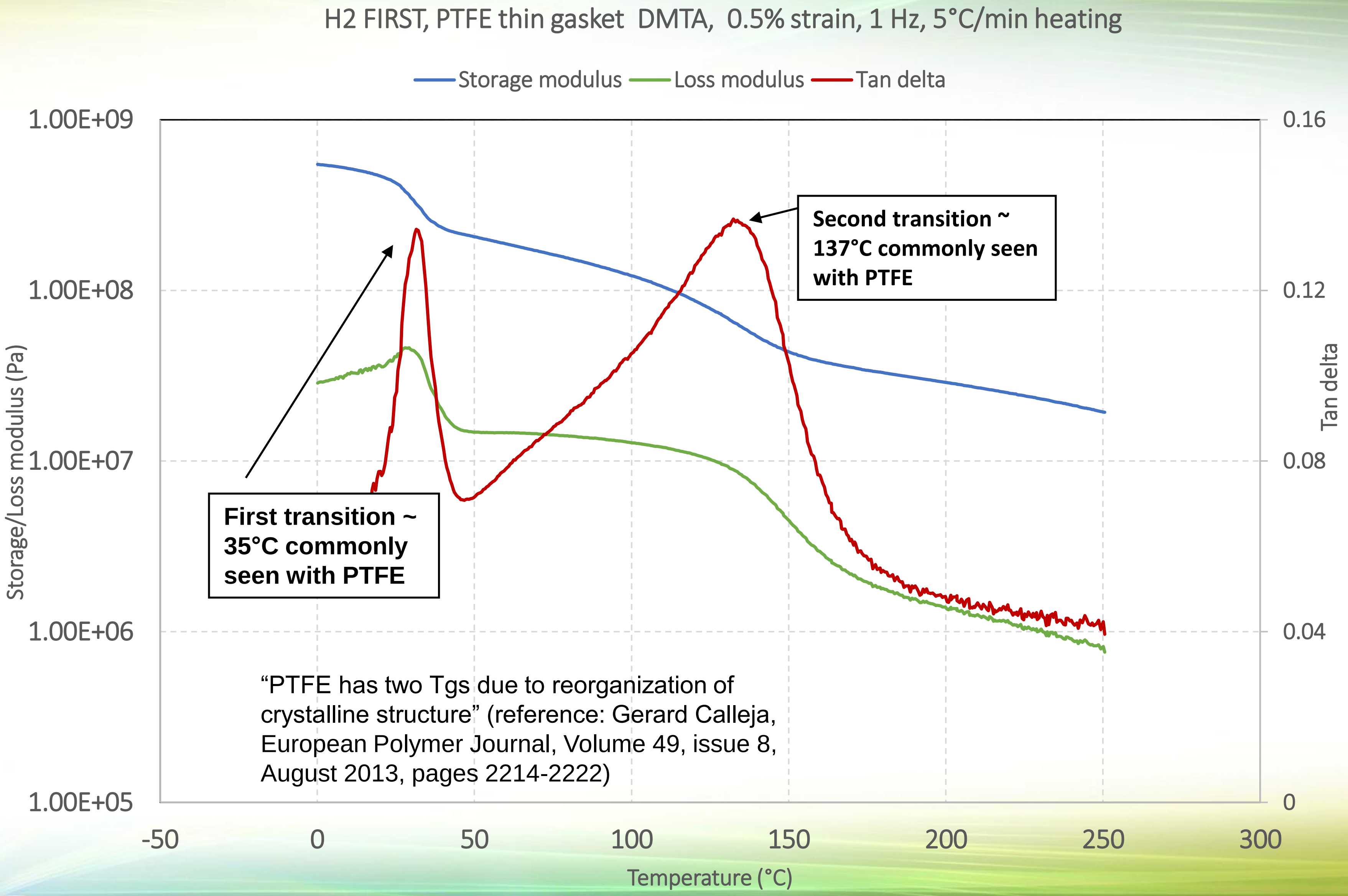




Thermal desorption spectroscopy

Suggestion of additional volatility after Ar/H2 exposure

Example of chemical identification of polymers using DMTA



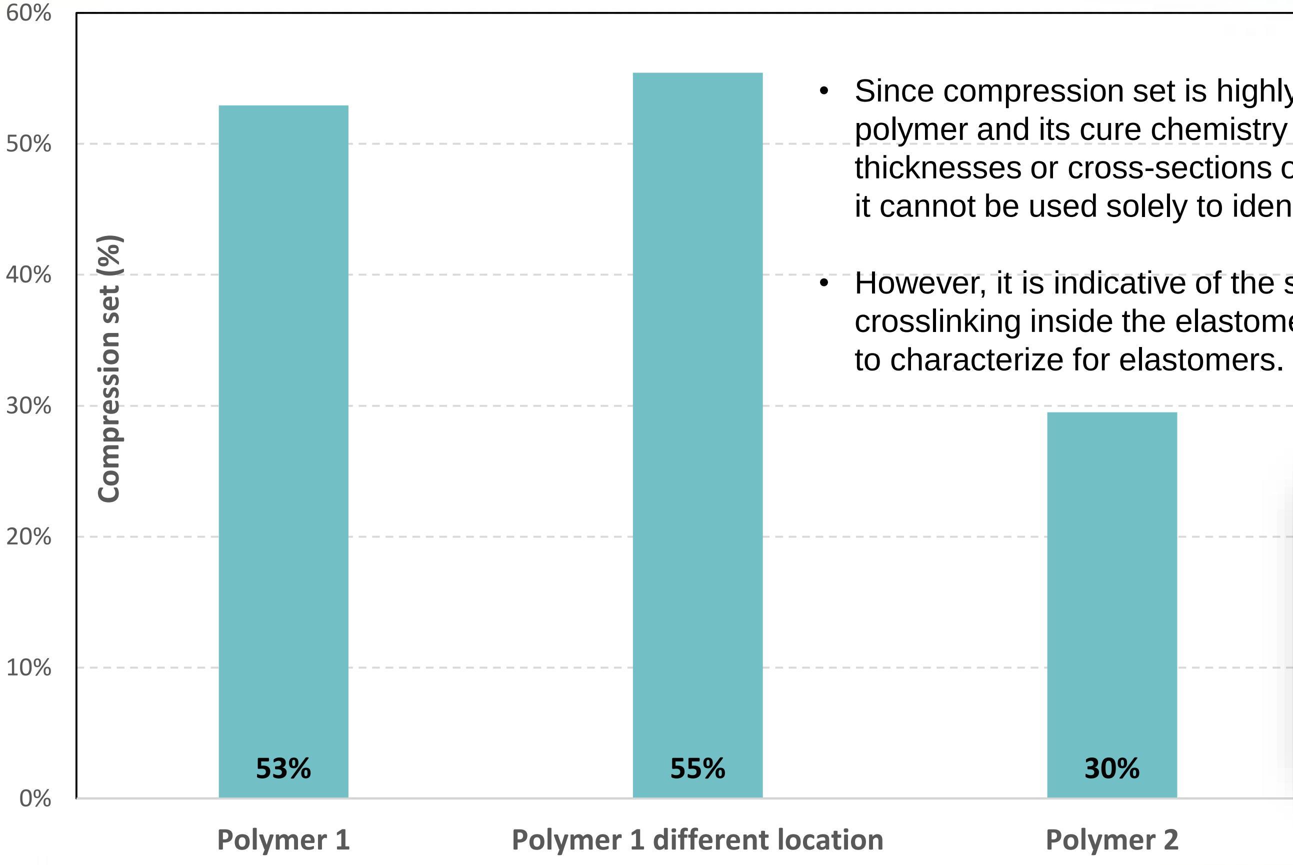
Second transition ~ 137°C commonly seen with PTFE

First transition ~ 35°C commonly seen with PTFE

"PTFE has two Tgs due to reorganization of crystalline structure" (reference: Gerard Calleja, European Polymer Journal, Volume 49, issue 8, August 2013, pages 2214-2222)

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

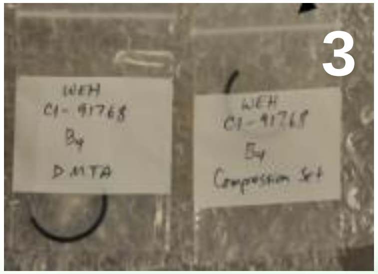
Compare to unexposed polymer properties for failure modes, technical basis for the same

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

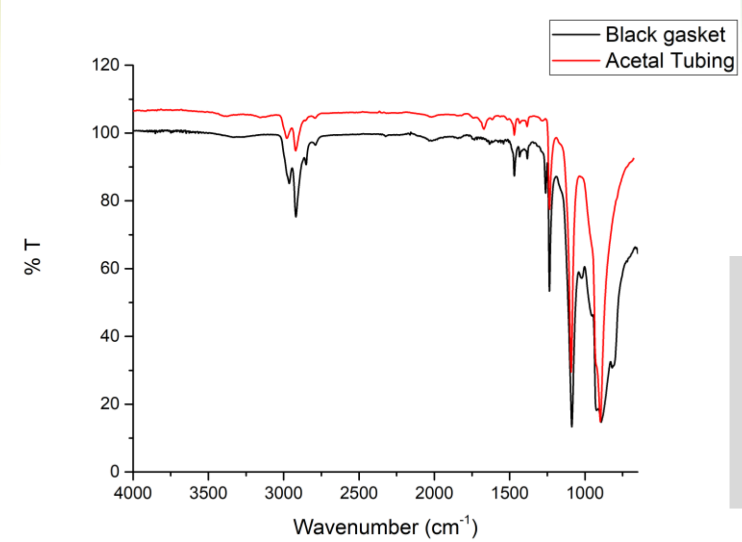
Fueling nozzles

Filters

Five different components from six suppliers

First step: Identify O ring chemistry in components

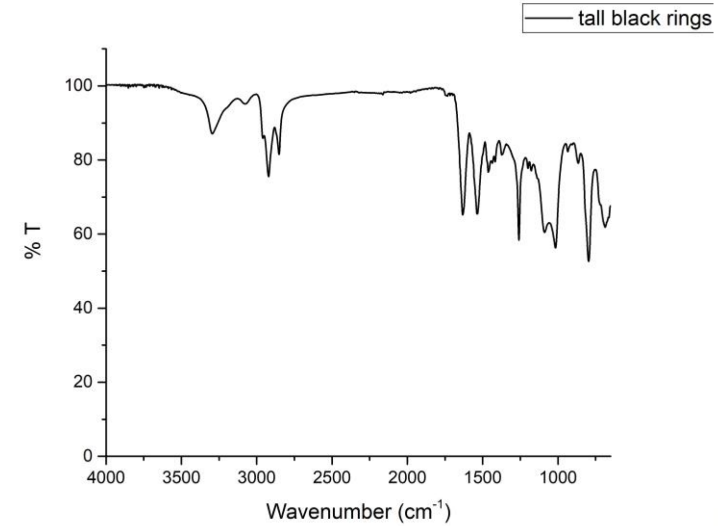
FT-IR spectra shown for manufacturer A Fueling Nozzle NREL FN001/2B



2B1 Black gasket

Acetal

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



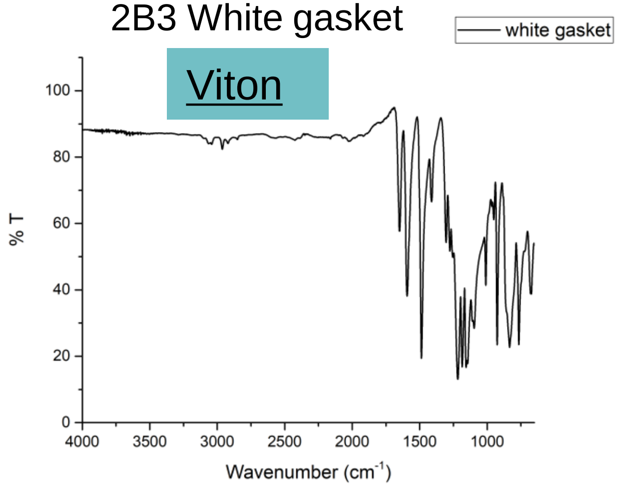
2B2 tall black ring

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

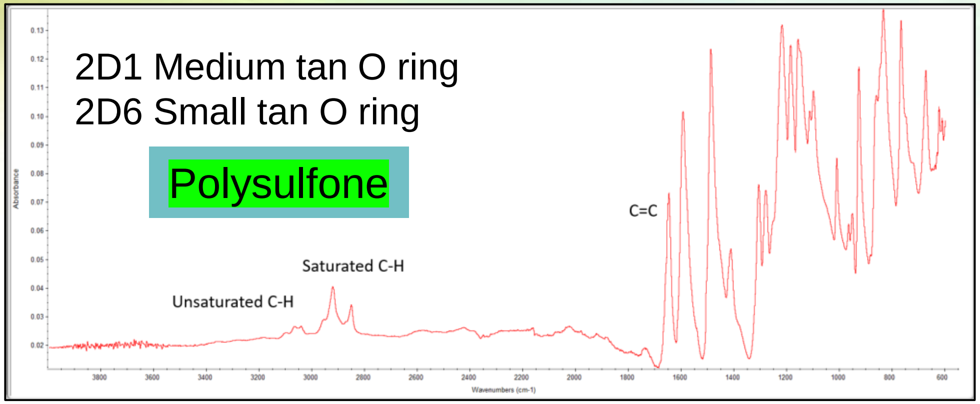


- Some C—H bands observed above 3000 cm^{-1} indicate unsaturated material
- C=C observed at 1651 cm^{-1}
- Further analysis of bands needed

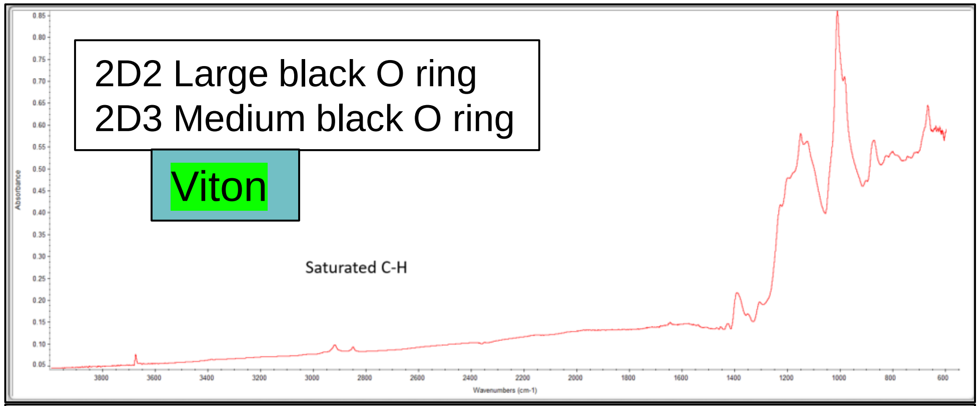
Different manufacturers of components use different polymers (compare to next slide)

Comparing O rings in similar components from Manufacturer B

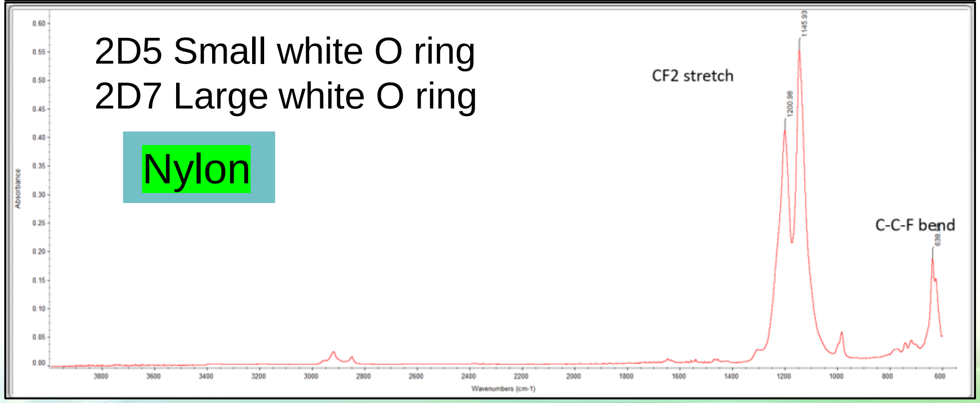
FT-IR spectra shown for manufacturer B Fueling Nozzle NREL FN050/2D


2D1 Medium tan O ring
2D6 Small tan O ring

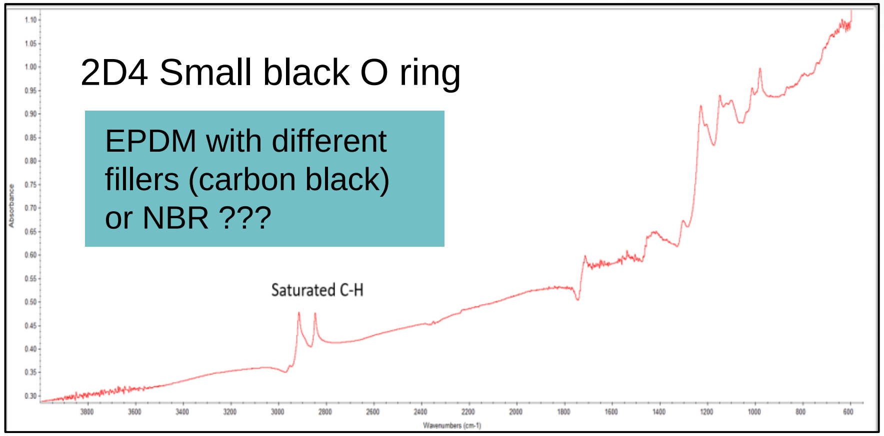
Polysulfone


2D2 Large black O ring
2D3 Medium black O ring

Viton


2D5 Small white O ring
2D7 Large white O ring

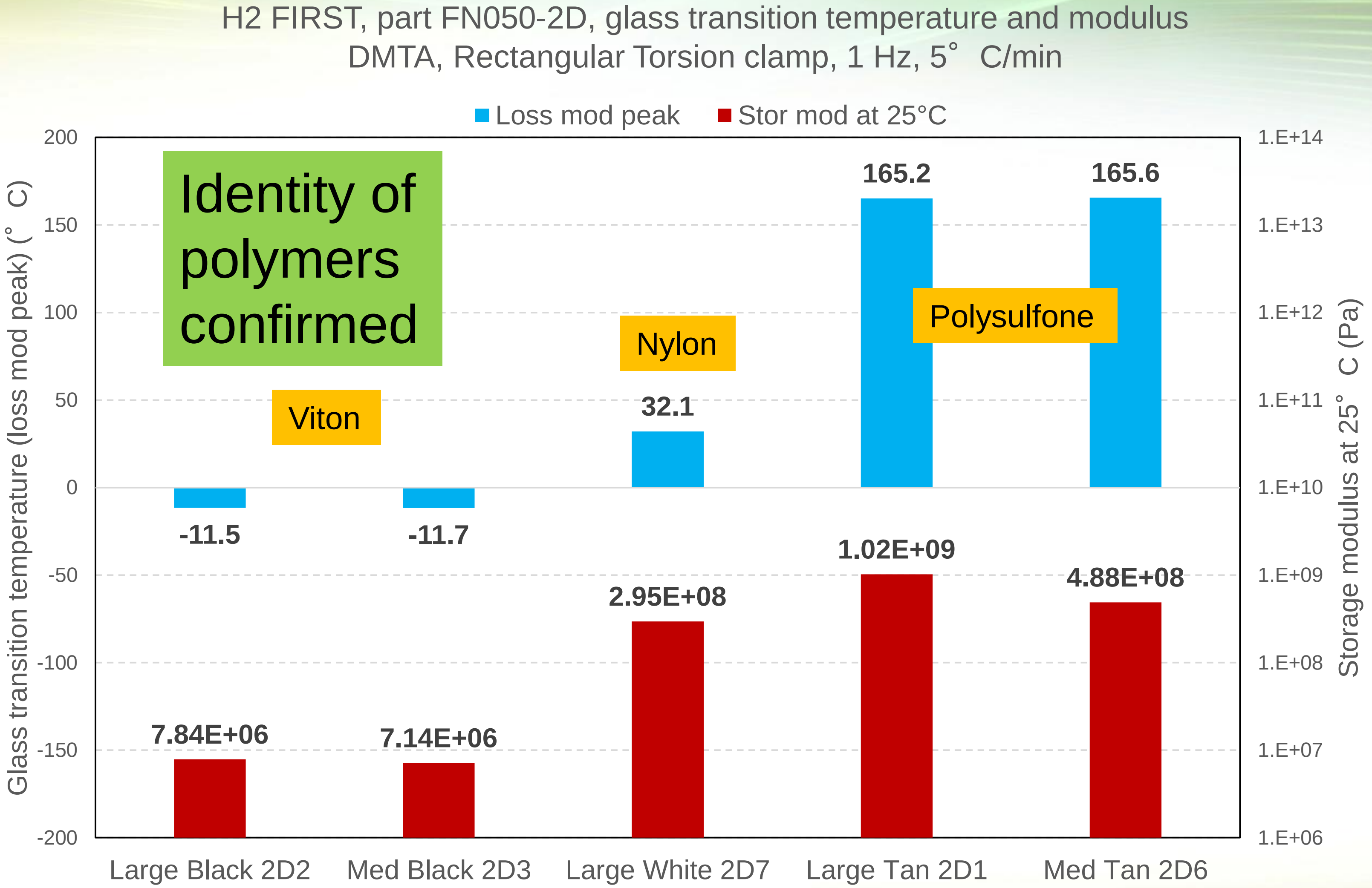
Nylon


2D4 Small black O ring

EPDM with different fillers (carbon black) or NBR ???

- 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)

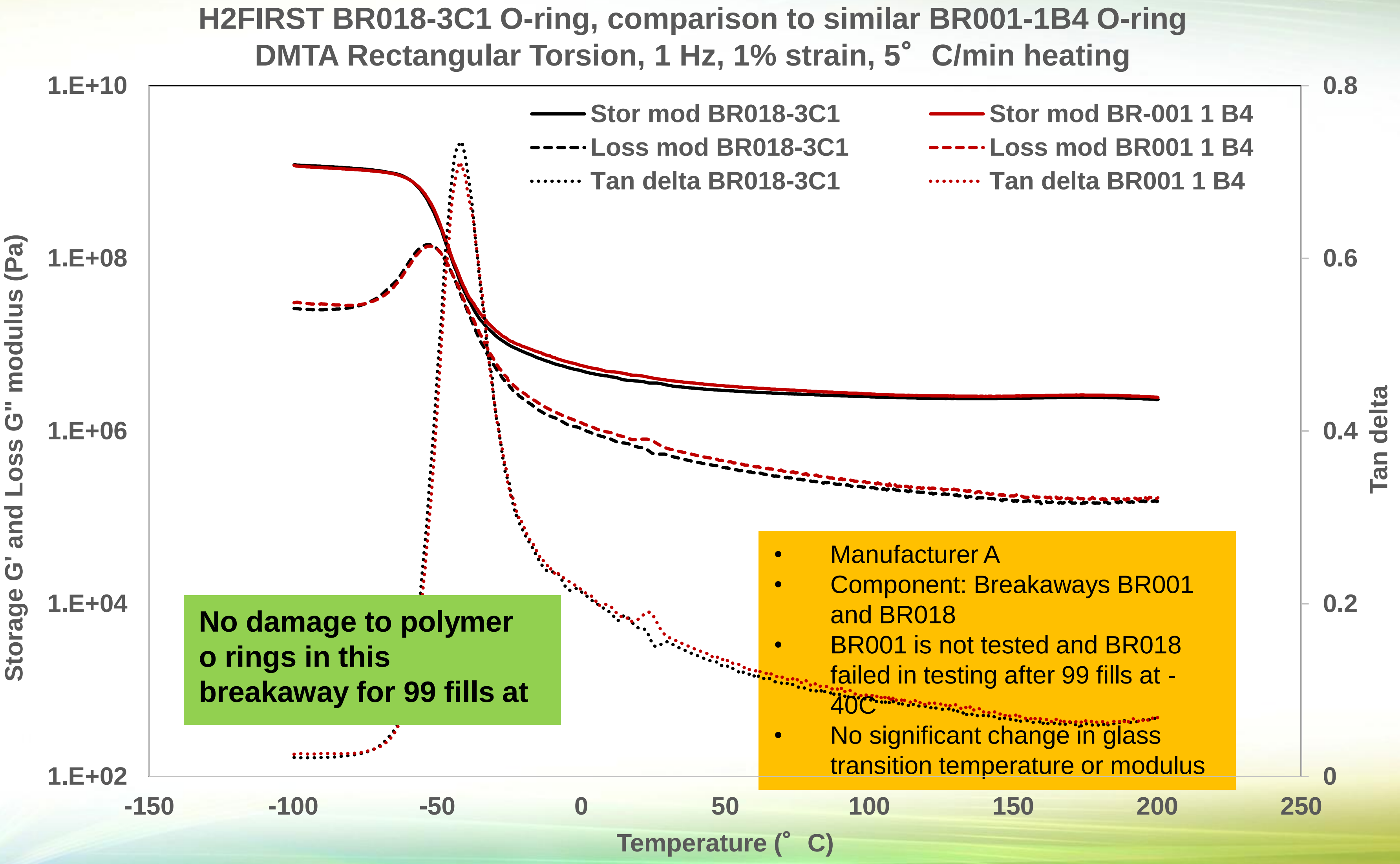
Failed components received from NREL

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.

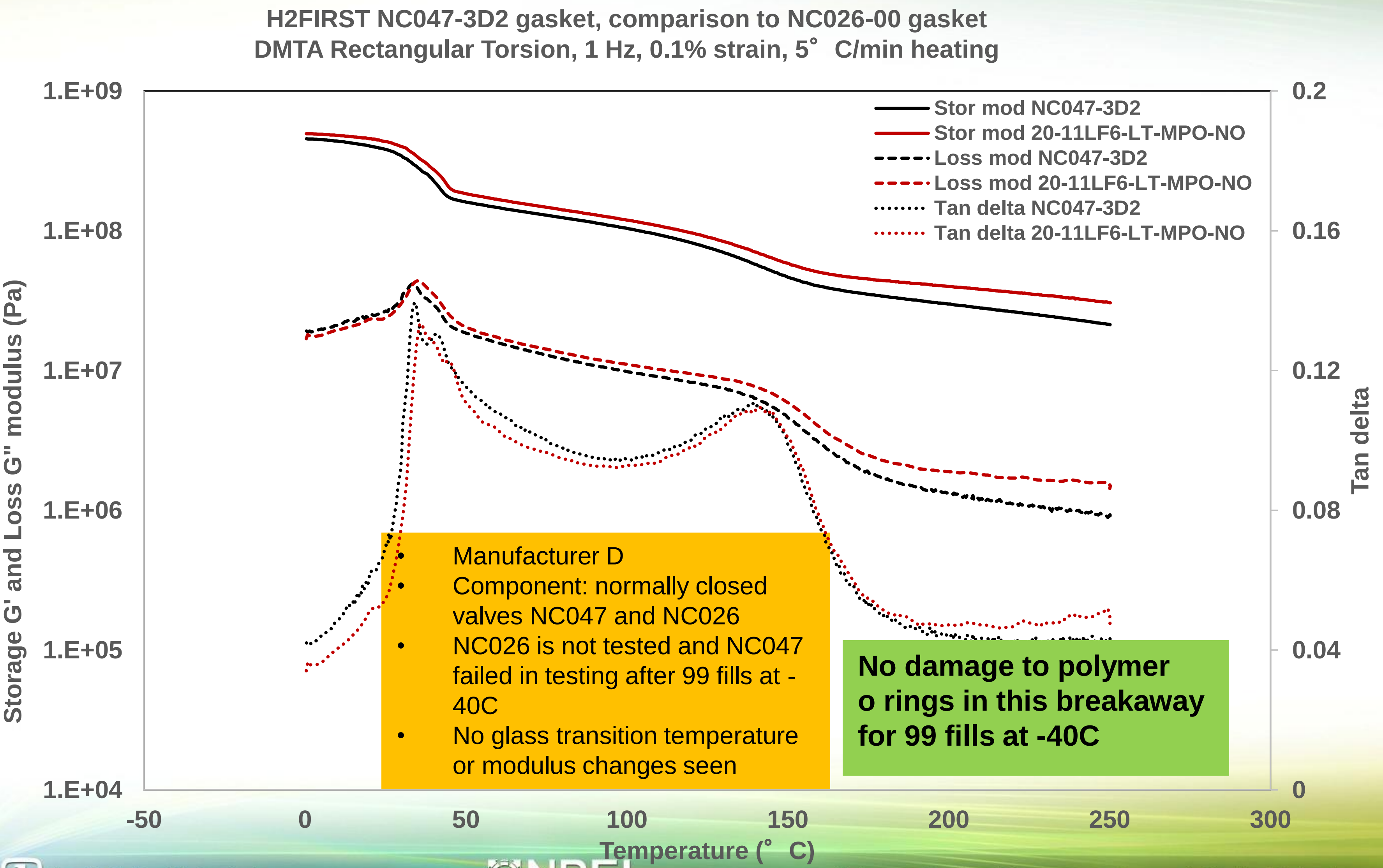
Comparison of polymers before and after exposure in breakaways (Example 1)


H2FIRST BR018-3C1 O-ring, comparison to similar BR001-1B4 O-ring
DMTA Rectangular Torsion, 1 Hz, 1% strain, 5° C/min heating

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)


H2FIRST NC047-3D2 gasket, comparison to NC026-00 gasket
DMTA Rectangular Torsion, 1 Hz, 0.1% strain, 5° C/min heating

- 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

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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