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Hydrogen Fueling Infrastructure Research and Station Technology

2020 DOE Hydrogen and Fuel Cells Program Review presentation

Dispenser Reliability: Materials R&D

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Overview

TIMELINE

- **Start date: 10/1/2016**
- **End date: 09/30/2020***

* Project continuation and direction determined annually by DOE

BARRIERS

Multiyear RD&D Barriers
Technology Validation Barriers

- **D.** Lack of Hydrogen Refueling Infrastructure Performance and Availability Data
- **E. Codes and Standards -** Validation projects will be closely coordinated with Safety, Codes and Standards

BUDGET

Project funding:

- **NREL**
  - FY19: $266k (carryover)
  - Project Total: $1,740k
- **SNL**
  - FY19: $590k
  - Project Total: $677k

PARTNERS

Funded

NREL: Hardware testing and lifetime analysis

SNL: Material Characterization

Close Collaboration

Walther-Präzision GmbH & Weh GmbH: Material consulting and lifetime monitoring

Materials compatibility testing steps

<u>Component Testing</u>

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

Failed and non-failed components

Survival analysis

<u>Unexposed Components</u>

Characterization of polymers retrieved for chemical identity

Database of baseline properties for unexposed polymers

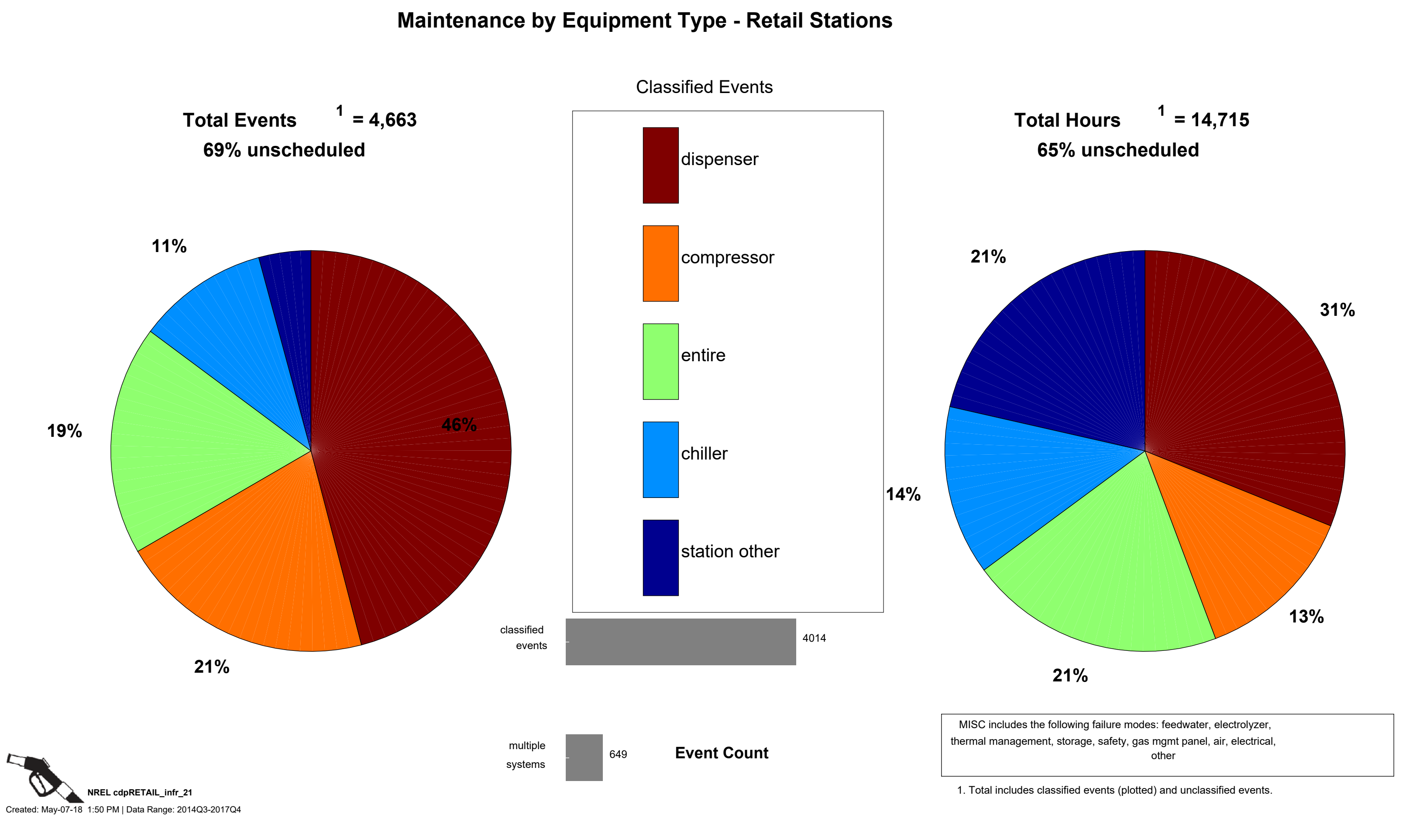
<u>Exposed components</u>

Characterization of exposed polymers

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

Relevance: Dispensers are #1 in Downtime

Dispensers are the top cause of maintenance events and downtime at retail hydrogen stations



Relevance

Objective: Assess 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

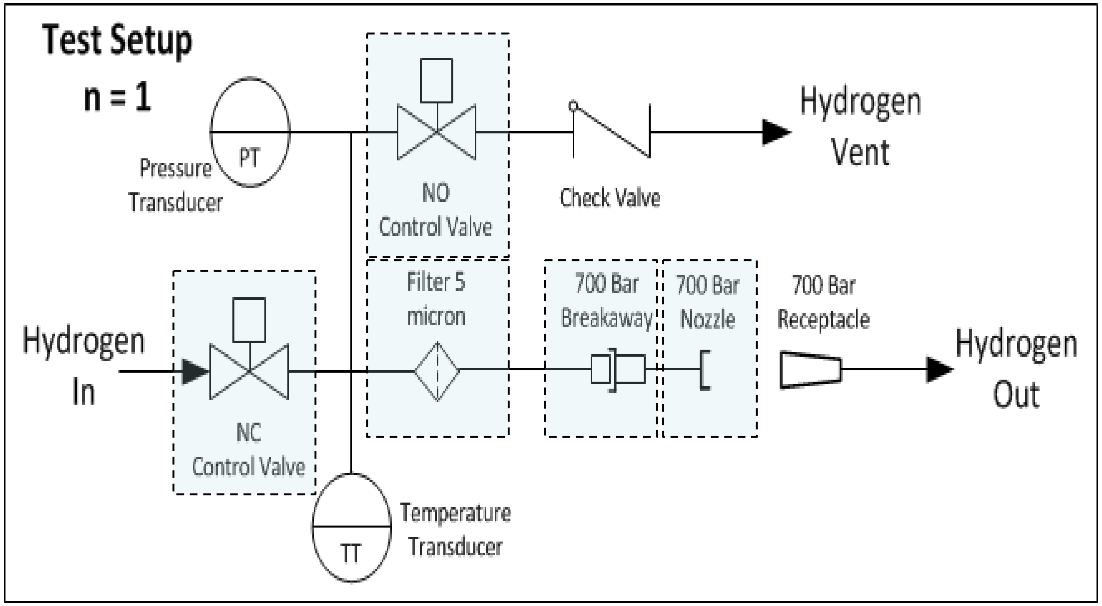
Multi-year Barriers RD and D	SNL Impact
D. Lack of Hydrogen Refueling Infrastructure Performance and Availability Data • Only qualitative information available from earlier test campaigns on performance of piping components at fueling dispenser conditions • Results of specific qualification tests do not assess effects other than pass/fail	• Material compatibility analyses pre-and post-exposure to hydrogen under dispenser operating conditions • Chemical and physical characterization of polymeric O-rings from failed and non-failed components to explore hydrogen effects • Dispenser reliability and lifetime prediction based on failure modes and degradation analyses

Approach: Accelerated Reliability Testing at NREL

Measure the 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):

Nozzles, breakaways, normally closed valve, normally open valve, filter



Material analysis of polymeric O-rings from actual tested components to establish causes of failure modes and predict component lifetimes and dispenser reliability

* = Due to fueling practicality, budget, and schedule the team limited the testing to two temperature levels: -40°C and -20°C

Approach: Test factors and response variables for NREL testing

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Fixed Factors
Controlled
H_2 pressure ramp rate (> 17.6 MPa/min)
H_2 flow rate (0.8 kg/min)
H_2 pressure range (14.7-77.9 MPa)

Variable Factors			
Controlled		**Uncontrolled**	
H_2 temperature	-40°C, -20°C	Ambient temperature	10°C - 40°C
Component types	Nozzles Breakaways NO valves NC valves Filters	Ambient humidity	0 - 100%

Response Variables	
H_2 leak (qualitative)	Yes or No
Fills before failure (quantitative)	Number
Amount of H_2 through component before failure (quantitative)	Kilograms

Some unknowns

- **Proprietary nature of polymeric materials per component type, different for different components – proper chemical identification of polymer needed**
- **For a given component design, identification of polymers' locations exposed to hydrogen – schematic of the component proprietary**

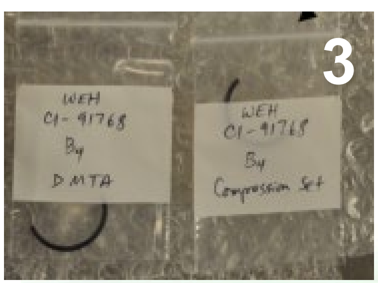
Approach: Polymer characterization on NREL tested components at SNL

- SNL's primary role –Support of NREL's ALTA testing of components for materials level testing of unexposed and failed components for failure mode and degradation analyses
- Total of 69 tested components received: 11 unexposed for baseline , 32 (-40℃) and 26 (-20℃)
- Temperatures and number of cycles of test: -40℃, -20℃; 1000 + plus cycles for each
- Goal: To identify polymer chemistries vulnerable to cold H_2 cycling, failure modes for polymers common across all component types, manufacturers – degradation analyses
- Motivation: Elastomers and thermoplastics used as O-rings in H_2 service components – leaks possible due to:
  - Compression set at low temperatures leading to leaks as the temperature increases
  - Extreme temperature conditions - cold, brittle catastrophic failure
  - Combined influence of temperature, pressure, cycling times

1. **Tested components received from NREL**
2. **Disassembly to collect O-rings with SNL procedure**
3. **Labeling O-rings and database entry**
4. **Chemical characterization and failure modes**
5. **Degradation analyses**

Approach: Disassembly of components at SNL

Walther Präzision nozzle



O-rings from WEH, Inc.

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 bagged individually and assigned special combination of letter and number to indicate component source, entered into database
4. Polymer pictures taken and stored along with whole component pictures
5. Specimens subjected to non-destructive testing first, followed by destructive testing

Approach: Post-H_2 characterization methods for polymer degradation assessment

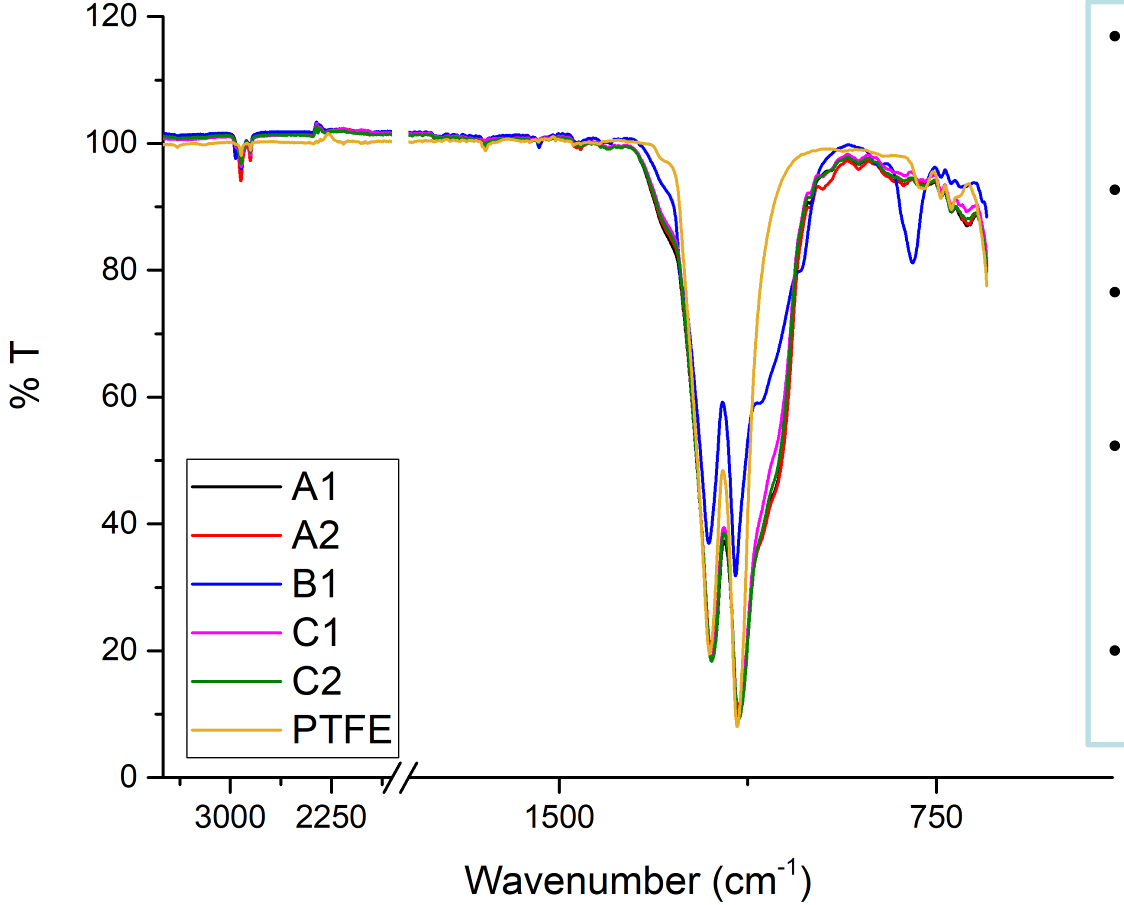
- **Microscopy (Non-destructive)**
  - Optical (Keyence) – blisters, external cracks, surface roughness/texturing, damage in the form of bubbles and/or tears or shredding
  - Assessment for permanent damage
- **Hardness (Non-destructive)**
  - Nano indentation for surface hardness and modulus changes due to H_2 exposure
  - Hardness changes are permanent; causes are plasticization or stress hardening of the matrix
- **Chemical characterization**
  - Fourier-transform infrared (FTIR) spectroscopy – polymer microstructure changes through functionalities identification **(Non-destructive)**
  - Dynamic mechanical and thermal analysis (DMTA) – T_g (glass transition temperature) changes and modulus changes **(Non-destructive)**

Multi-technique characterization is necessary for identification

For e.g. Collection of FTIR-ATR spectra for elastomers is challenging but combined with T_g /modulus data from DMTA, confirmation of chemical changes possible

Keyence images of typical damage seen in polymer O rings after H_2 gas exposure

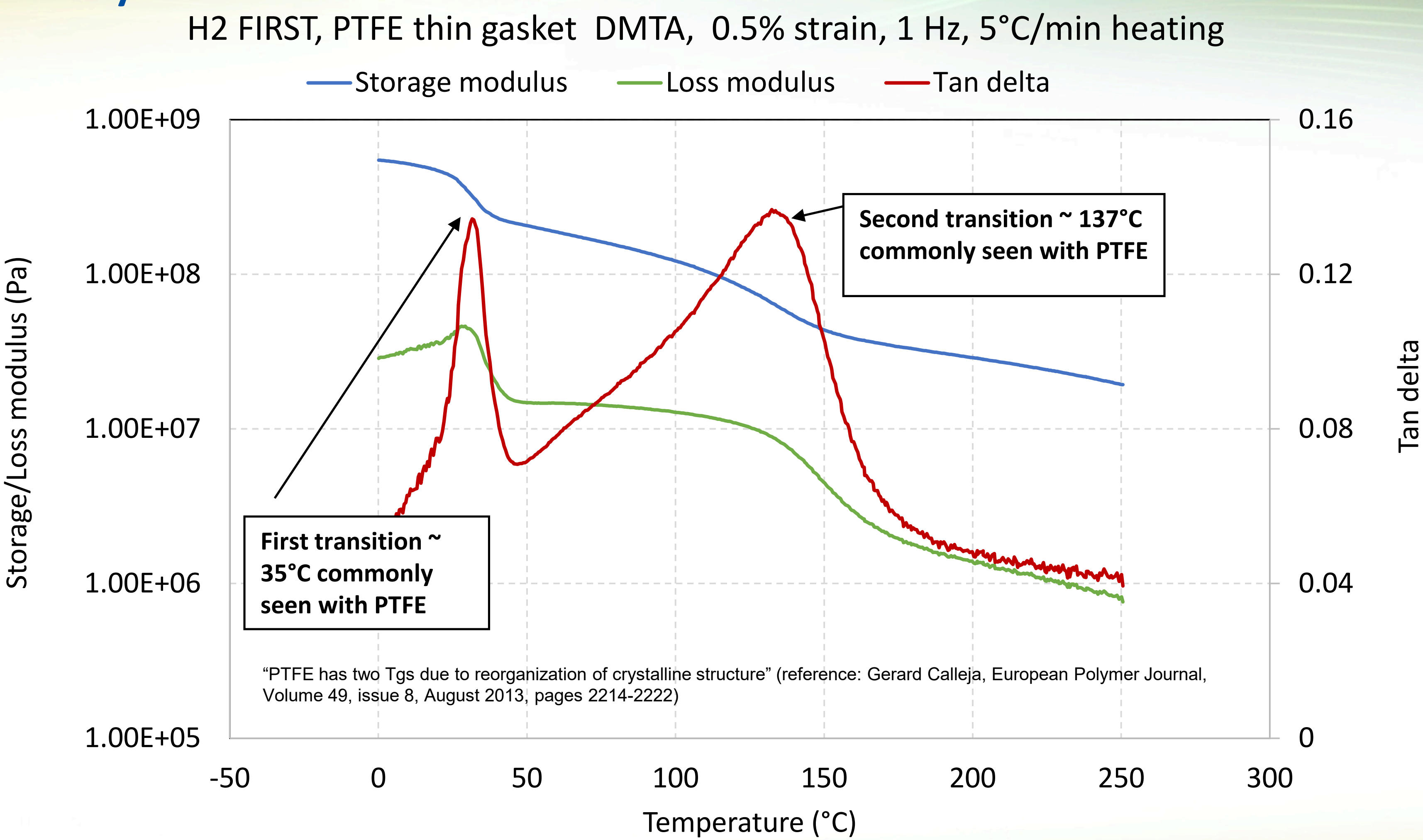
Approach:
IR spectroscopy to detect O-ring chemistry changes



- Material characterization with Infra-red spectroscopy ATR (attenuated total reflectance)
- Non-destructive, surface-focused technique
- Precise identification possible in unique fingerprint region (1500 to 500 cm^{-1})
- Assess complex bending, rotational and vibrational modes of molecular motion in response to IR, unique to each material type
- Elastomeric materials give weak signals, still discernable

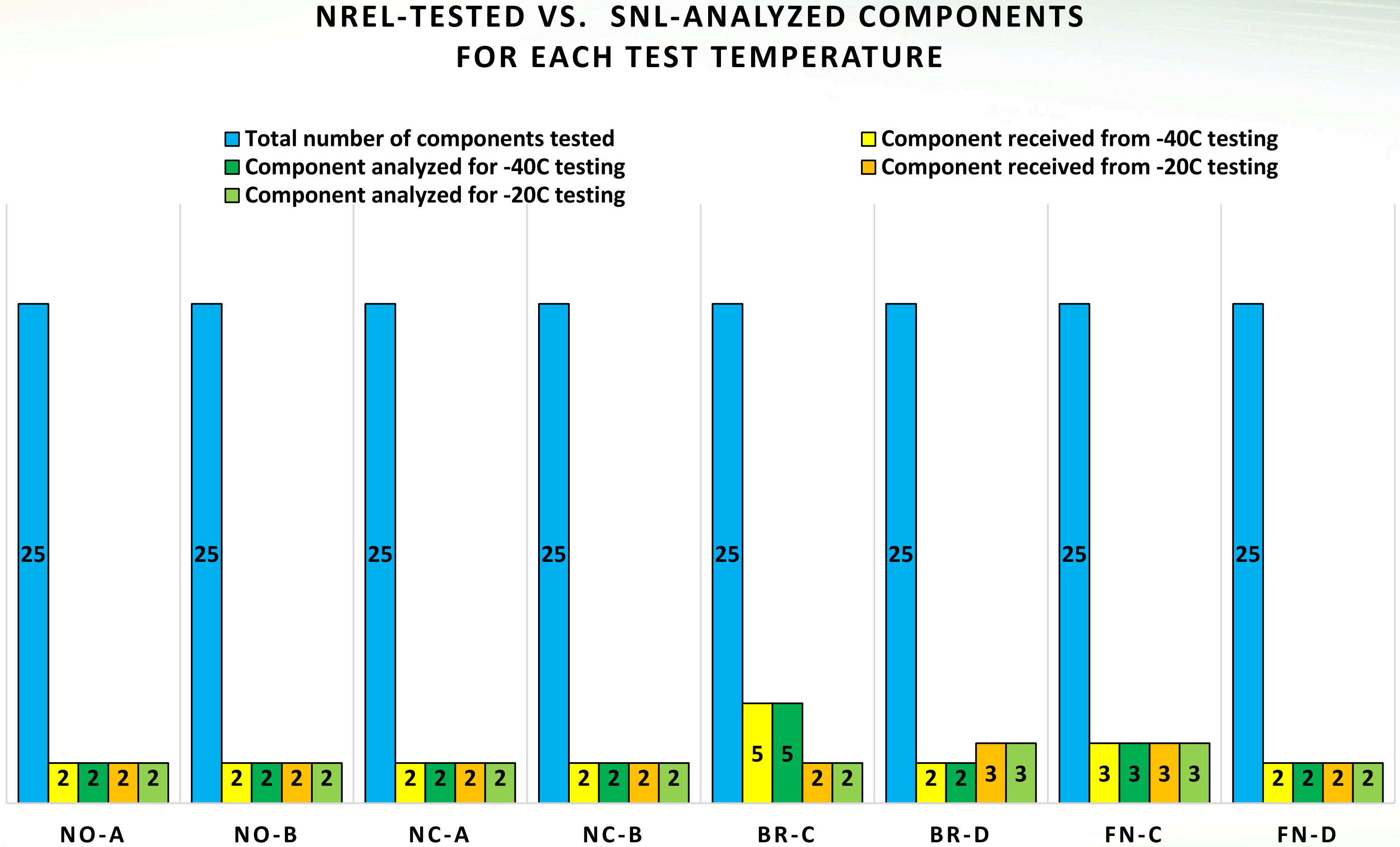
For e.g.: in the figure shown, O-ring C2 **(green)** compares well to a standard spectrum of PTFE **(orange)**

Approach:
Thermo-mechanical property measurements (DMTA) for changes in chemistry



Glass transition temperature and modulus shifts reflect polymer microstructural changes in response to exposure to H_2

Accomplishment:
Analyses of tested components



NO = normally open, NC =normally closed, BR = breakaways FN = fueling nozzles
A, B, C and D stand for protected manufacturer IDs

Accomplishment:
Polymers identified in tested components

Component*	NO Valves		NC Valves		Breakaways		Fueling Nozzles	
Polymer (numbered series)	NO-A (1-25)	NO-B (25-50)	NC-A (1-25)	NC-B (25-50)	BR-C (1-25)	BR-D (25-50)	FN-C (1-25)	FN-D (25-50)
Components analyzed/tested	8/25	8/25	8/25	8/25	14/25	10/25	12/25	8/25
PTFE								
NBR								
PEEK								
FKM								
Polyurethane PURs								
Butyl Rubber								
Neoprene								
POM								
HNBR								

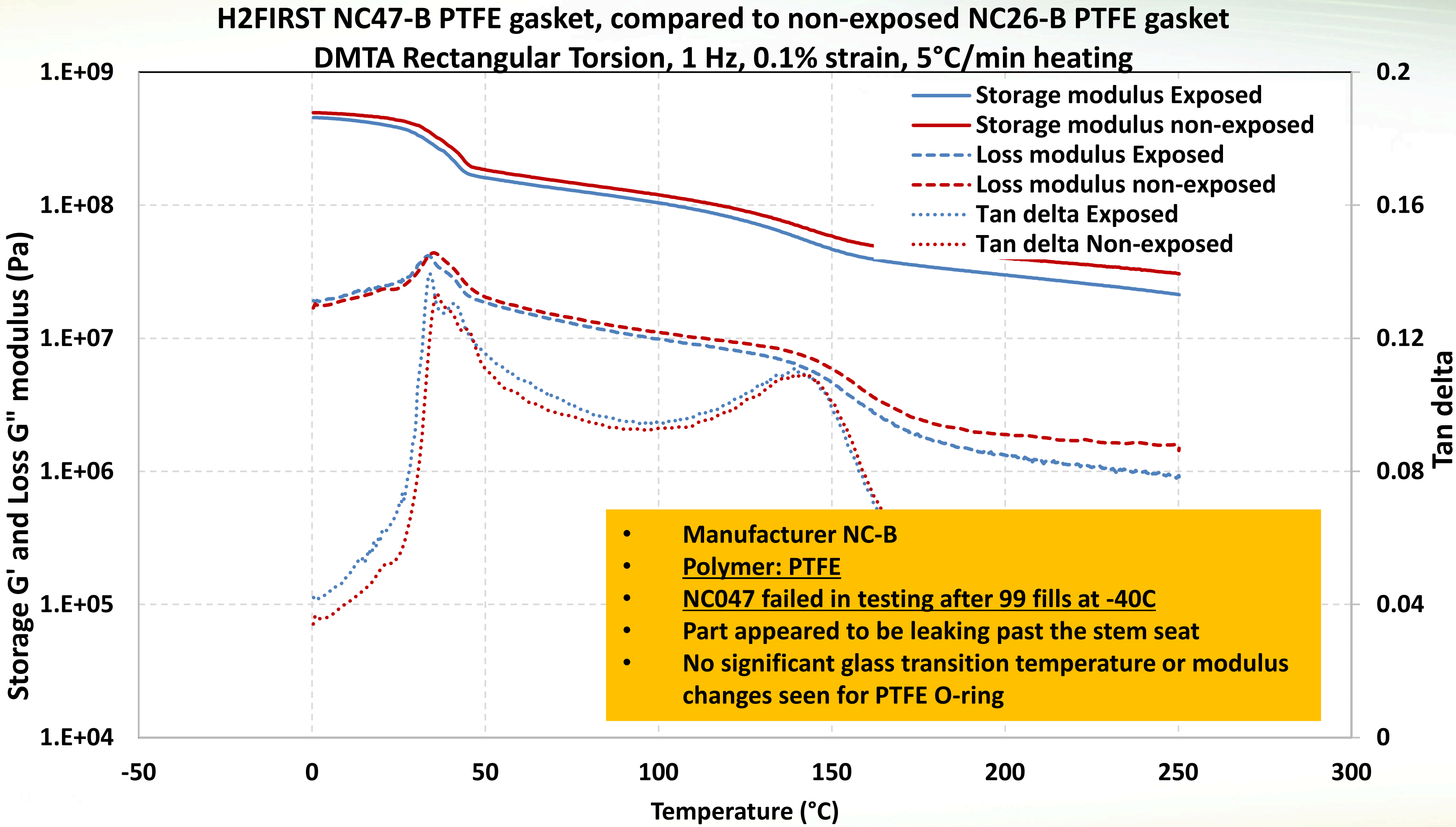
*= manufacturer ID protected

Polymer susceptibility to damage in testing depends on

- **Chemistry of polymer selections and changes in microstructure due to H_2 exposure**
- **Exposure and cycling at low temperatures (-40℃ vs -20℃) and related thermal shock**
- **Number of cycles (1000 vs 500) and corresponding mechanical physical stress**
- **Design related factors - location within component dictates**
  - **Whether polymer exposed to H_2 when in service**
  - **How metal fixturing makes seal with polymer, moves relative to polymer, etc.**

Accomplishment:

DMTA demonstrates that polymer chemical properties changes are <u>not responsible</u> for early failure of PTFE in normally closed valves NC-B valves



- Manufacturer NC-B
- <u>Polymer: PTFE</u>
- <u>NC047 failed in testing after 99 fills at -40C</u>
- Part appeared to be leaking past the stem seat
- No significant glass transition temperature or modulus changes seen for PTFE O-ring

- **Insignificant change in PTFE glass transition temperature and modulus, therefore <u>not</u> directly responsible for NC valve failure**

Accomplishment:

Optical microscopy demonstrates change (degradation) in physical properties of failed normally closed valve PTFE O-rings

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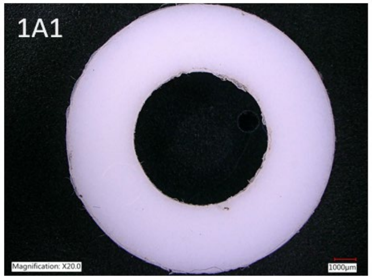
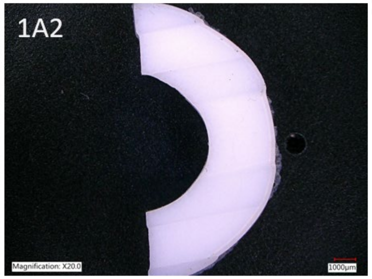
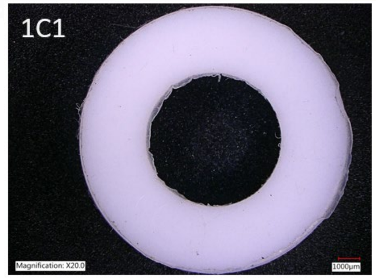
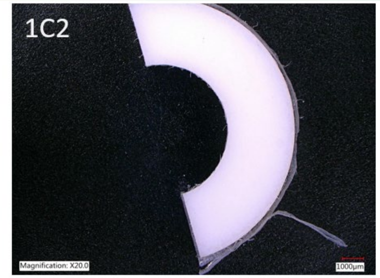
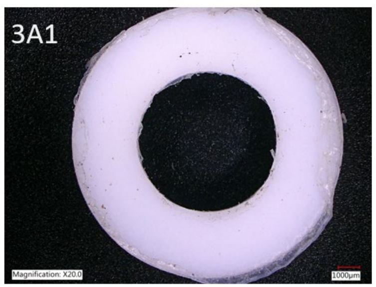


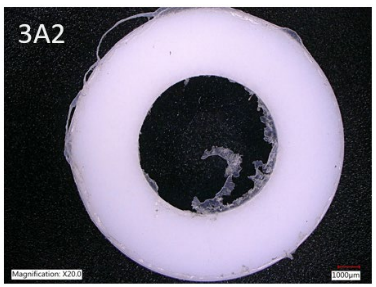




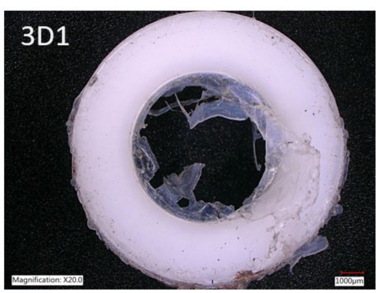


NC026-B:
non H_2 exposed





NC049-B:
H_2 exposed,
failed at 99
cycles, -40°C



NC047-B:
H_2 exposed,
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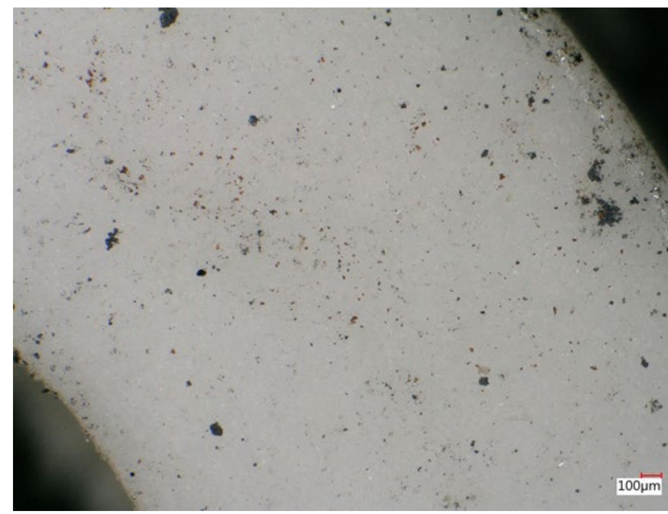
cycles, -40°C



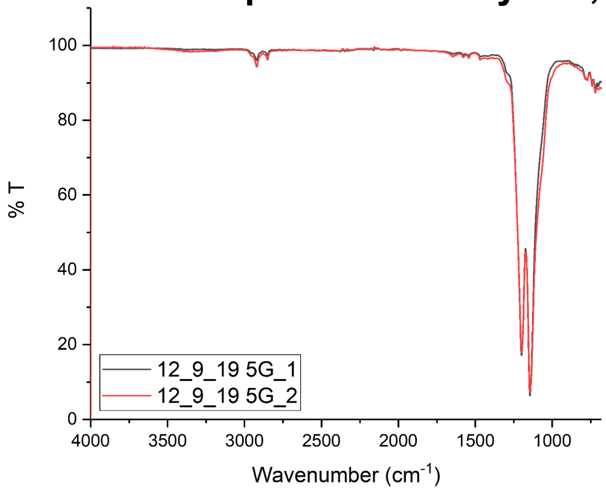
Metallic particles and
other debris embedded
in failed PTFE O-rings

Significant increase in fraying and deposit of metallic and non-metallic debris with H_2 exposure

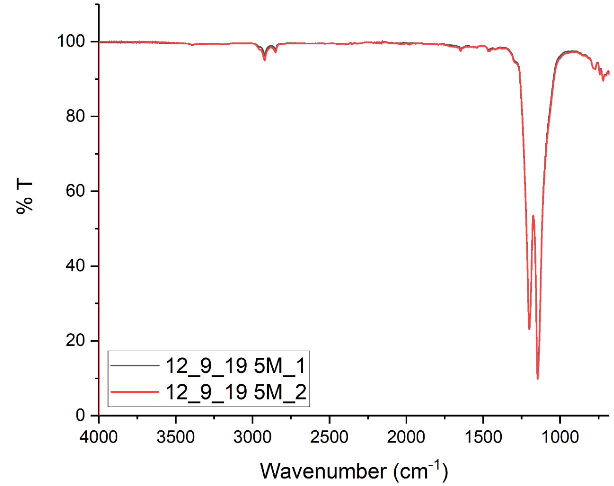
Accomplishment:

ATR-FTIR demonstrates no polymer chemical structural changes for PTFE O-rings in normally open valves NO-A after exposure to H_2

NO33-B passed 1000 cycles, -20°C

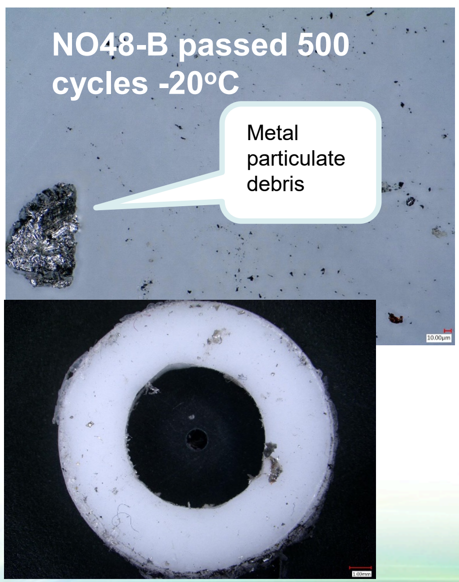


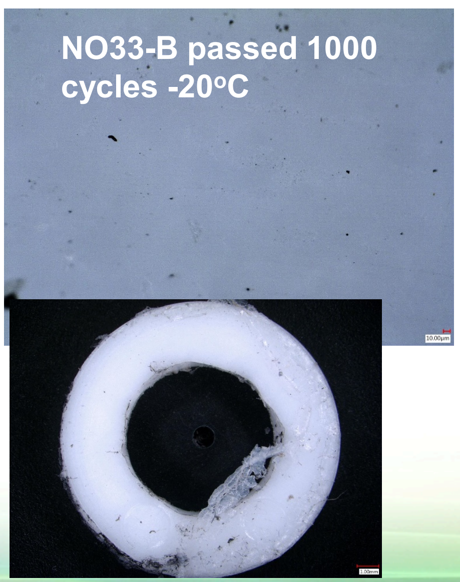
NO48-B passed 500 cycles, -20°C

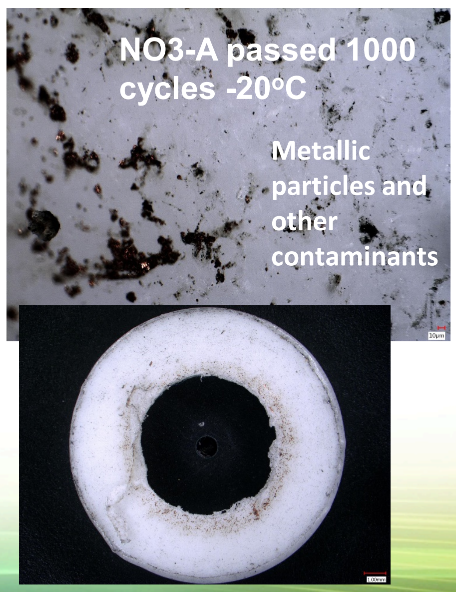


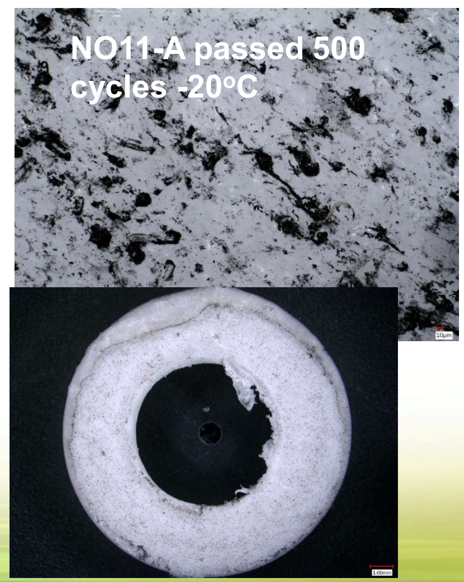
Optical microscopy evidence of damage

- PTFE O-rings in NO-A and NO-B show different types of damage
- The NO-B rings are cleaner but show greater fraying
- The NO-A PTFE show fraying and embedded metal particles and discolorations for the same number of cycles



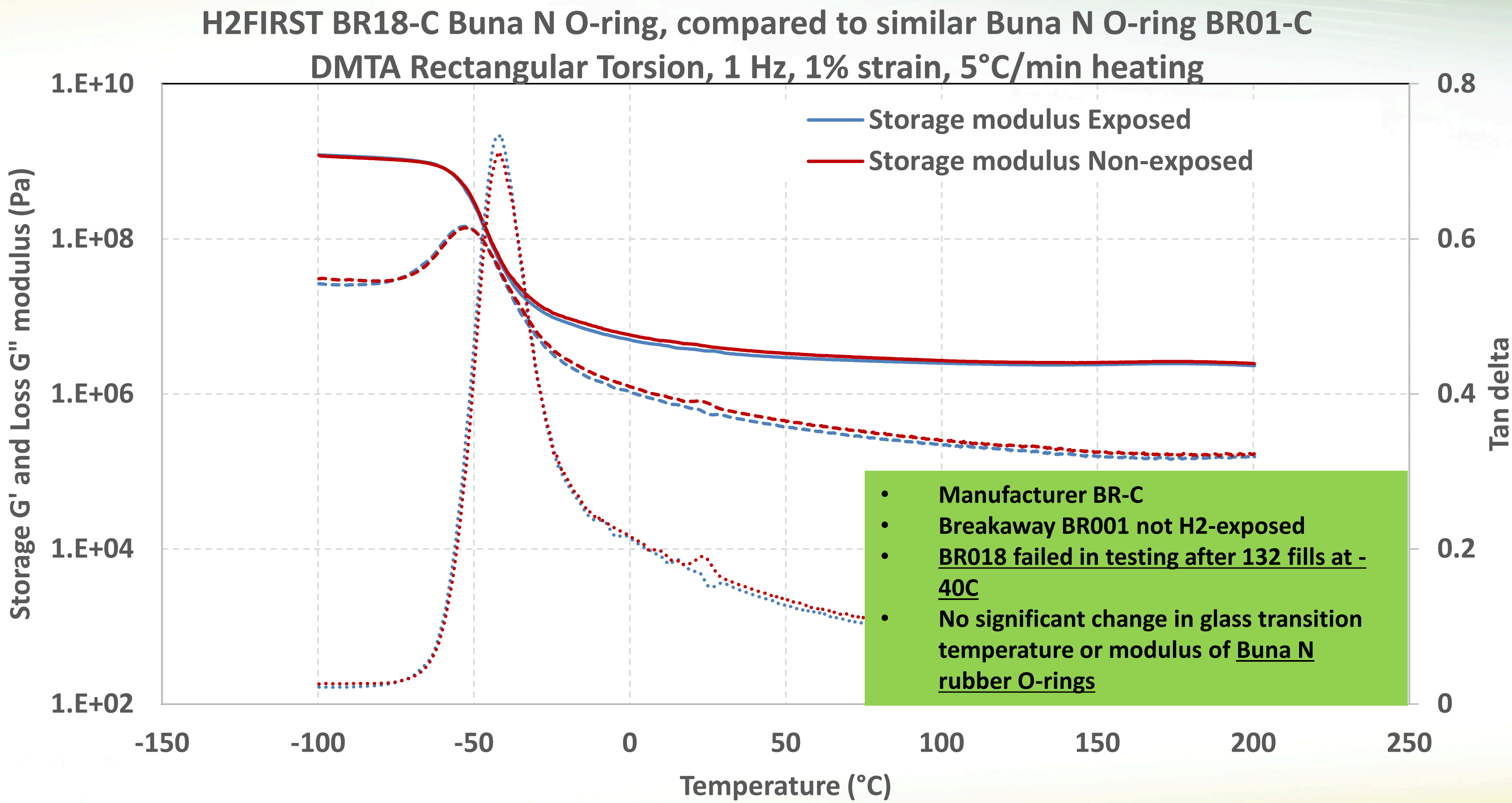






Accomplishment:

DMTA demonstrates that polymer chemical properties changes are <u>not responsible</u> for early failure of buna-n found in breakaway BR-C:

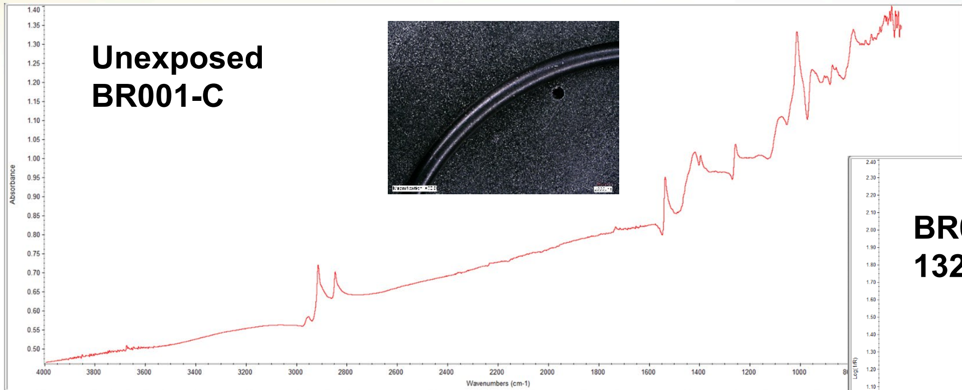


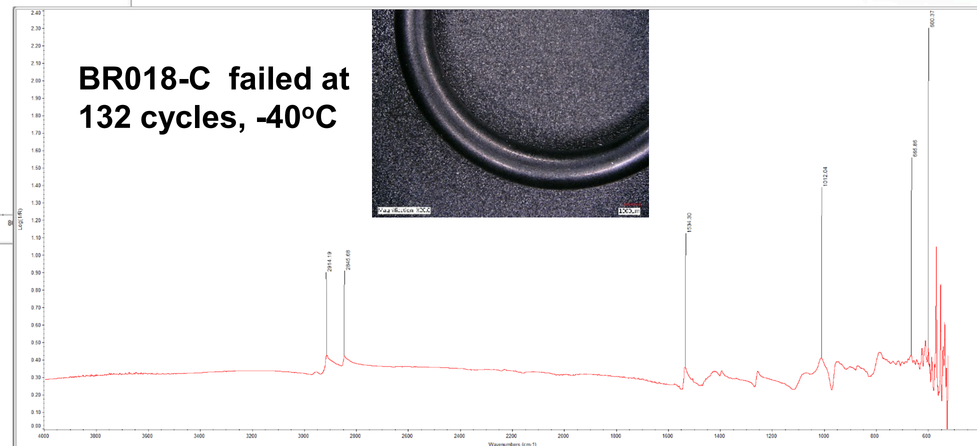
- Manufacturer BR-C
- Breakaway BR001 not H2-exposed
- <u>BR018 failed in testing after 132 fills at -40C</u>
- No significant change in glass transition temperature or modulus of <u>Buna N rubber O-rings</u>

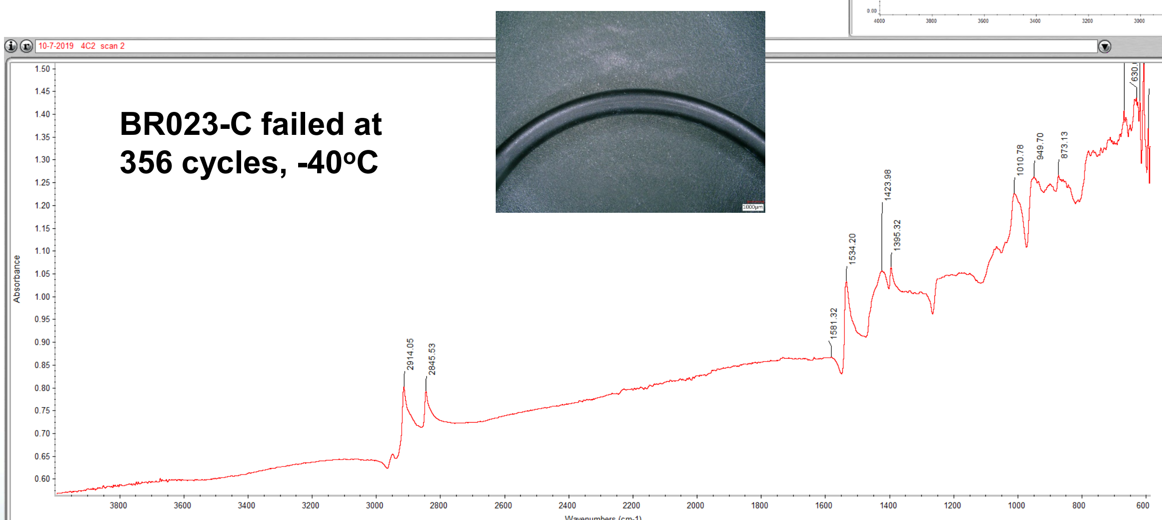
- Change in Buna N thermomechanical properties <u>not</u> reason for breakaway failure

Accomplishment:

ATR-FTIR demonstrates no polymer chemical structural changes for Buna-N O-rings in breakaway BR-C after exposure to H_2







- ATR-FTIR spectra for Buna O rings from these failed breakaways do not show significant chemical differences
- No physical damage seen with any of the Buna N O-rings in the optical images

Accomplishment:

Nano indentation shows PTFE physical property (hardness, modulus) changes
Optical microscopy shows degradation of multiple polymers in breakaways

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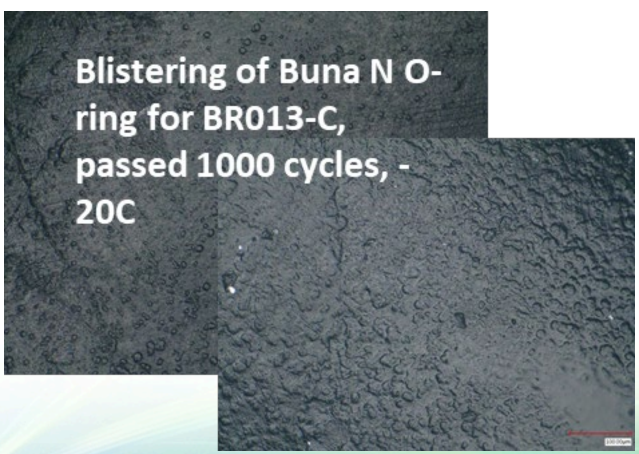
Nanoindentation of exposed and control PTFE O-rings from multiple components

Polymer physical property changes indicate either

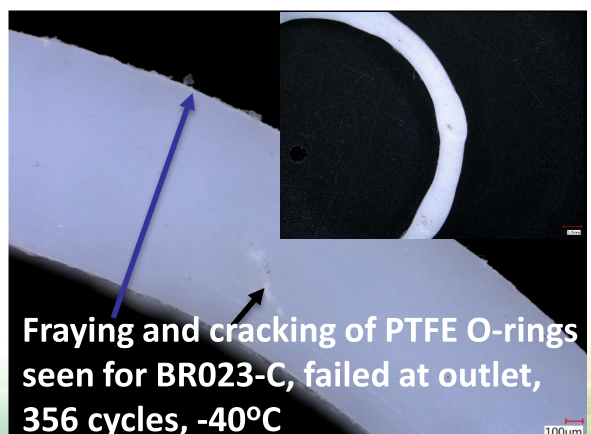
- plasticization (lowering of hardness modulus)
- stress hardening (increase in hardness) by H_2

Typical degradation effects seen for O-rings in this study

Breakaway BR-C	Hardness (GPa)	Modulus (GPa)	Hydrogen exposed?	Number of cycles @ failure, test temperature	Failure modes
BR001-C PTFE	0.11 ± 0.02	1.68 ± 0.24	No	NA	NA
BR018-C PTFE	0.07 ± 0.02	1.26 ± 0.18	Yes	132 cycles, -40ºC	Leak at outlet of breakaway coupling
Normally closed valve NC-B	**Hardness (GPa)**	**Modulus (GPa)**	**Hydrogen exposed?**	**Number of cycles @ failure, test temperature**	**Failure modes**
NC026-B	0.064±0.02	1.58±0.35	No	NA	NA
NC049	0.068±0.01	1.53±0.19	Yes	99 cycles, -40ºC	Leak at packing gland and stem interface
NC047	0.065±0.02	1.06±0.26	Yes	99 cycles, -40ºC	Leaking past stem seat



Blistering of Buna N O-ring for BR013-C, passed 1000 cycles, -20C



Fraying and cracking of PTFE O-rings seen for BR023-C, failed at outlet, 356 cycles, -40ºC

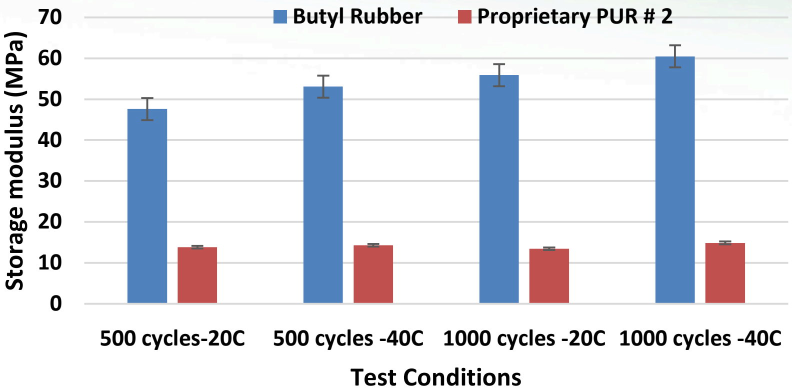
Flattening of the Buna N O rings with debris seen for BR023-C, failed at outlet, 356 cycles, -40ºC

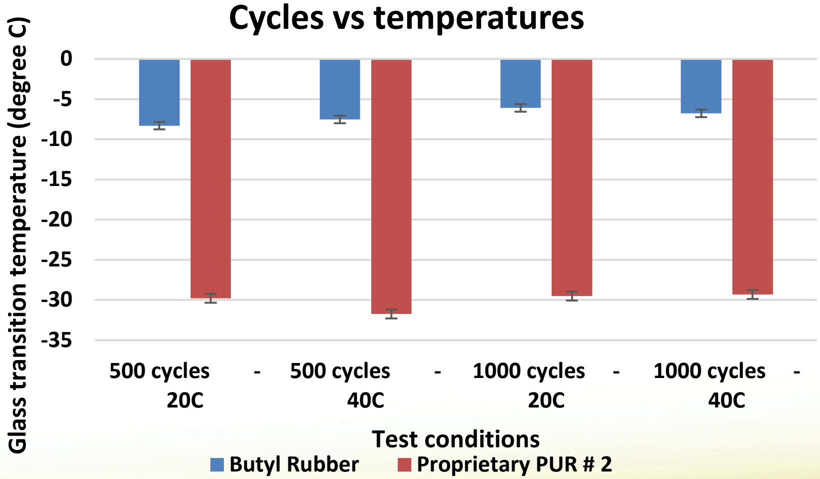
Accomplishment:

DMTA demonstrates chemical changes to butyl rubber in breakaway with trends based on number of cycles and exposure temperature

Breakaways	Polymer	Storage modulus (MPa)	Tan Delta Peak 1 (degree C)
BR031-D (1000 cycles, -40°C)	Butyl rubber	60.47±13.34	-6.77±0.44
	Proprietary PUR #2	14.87±0.49	-29.31±0.65
BR048-D (500 cycles, -40°C)	Butyl rubber	53.08±1.58	-7.53±0.07
	Proprietary PUR #2	14.30±0.66	-31.75±0.10
BR034-D (1000 cycles, -20°C)	Butyl rubber	55.9±8.4	-6.1±0.50
	Proprietary PUR #2	13.4±0.5	-29.5±0.40
BR056-D (500 cycles, -20°C)	Butyl Rubber	47.6±7.5	-8.3±0.4
	Proprietary PUR #2	13.80±0.90	-29.80±1.9

- All the BR-D breakaways passed under test conditions shown
- Storage modulus of butyl rubber O-rings increases with more cycles and lower exposure temperatures
- Glass transition temperatures are steady under test conditions

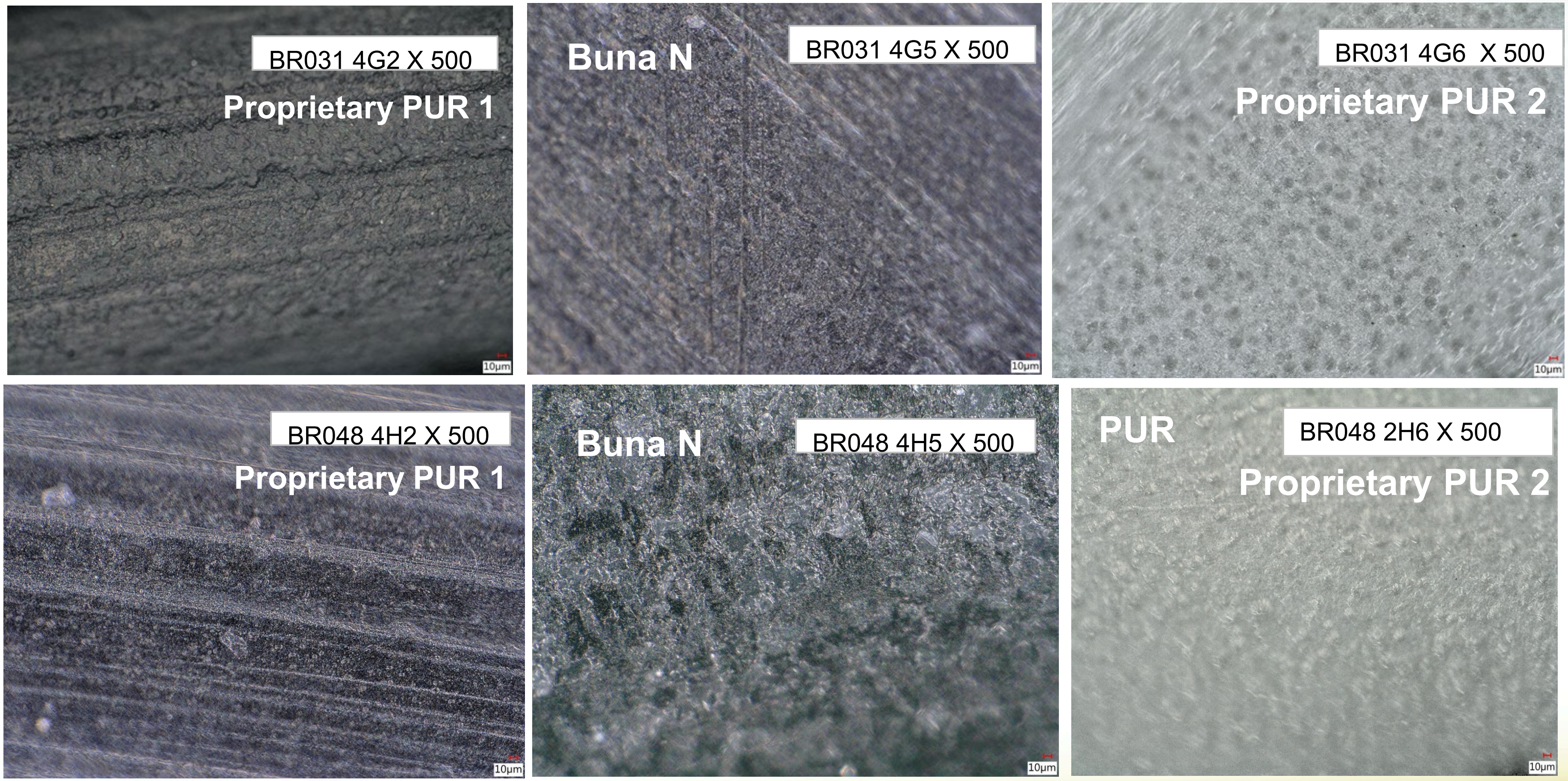




Accomplishment:

Optical microscopy shows increased blistering of Buna-N and increased wear of PUR with additional cycles

BR031-D (top row) passed 1000 cycles, -40C
BR048-D (bottom row) passed 500 cycles, -40C

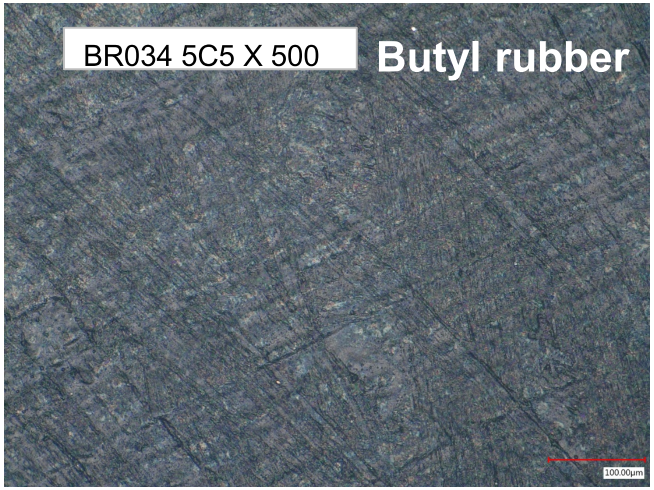


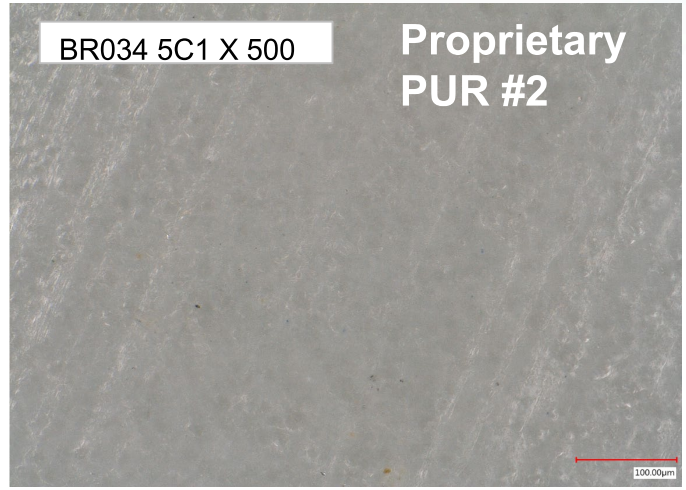
At -40C test temperature, blisters in Buna N, PUR# 2 and wear in PUR# 1 is greater at 1000 cycles vs 500 cycles
This indicates an effect of number of cycles: greater the number of cycles, greater the damage

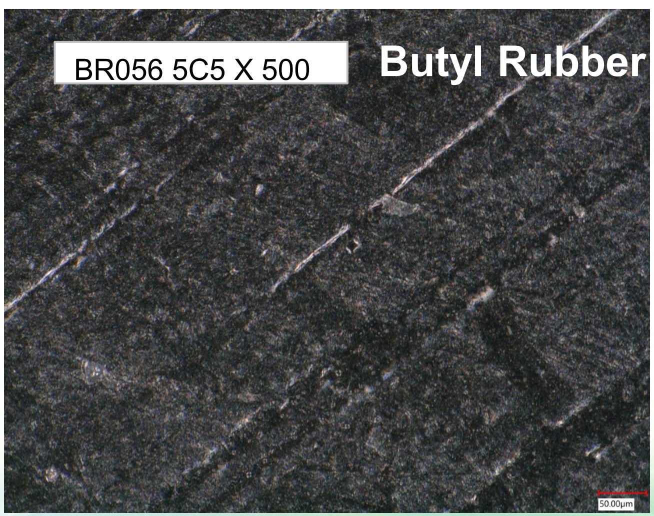
Accomplishment:

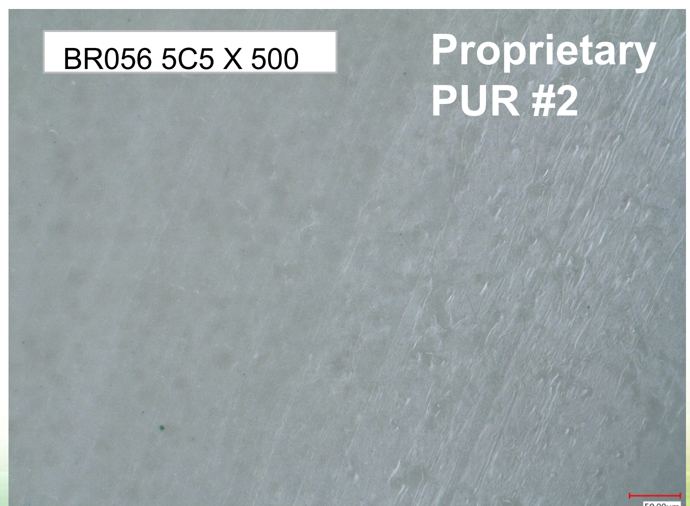
Optical microscopy shows less damage to polymers cycled at -20°C, independent of number of cycles

BR034-D (top row) passed 1000 cycles, -20°C
BR056-D (bottom row) passed 500 cycles, -20°C





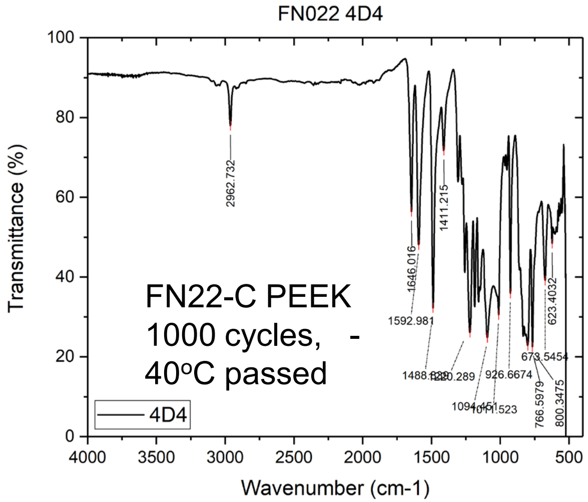


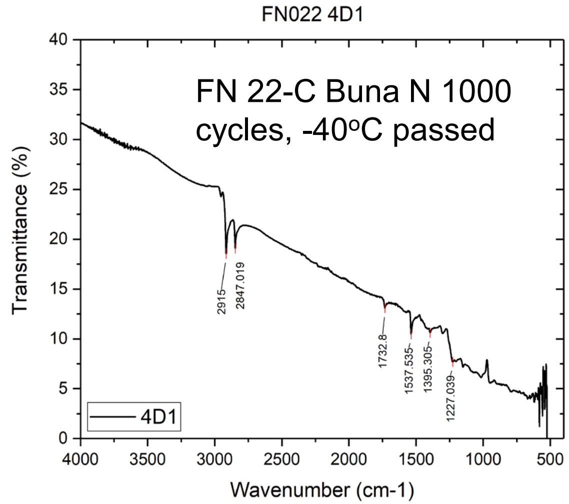


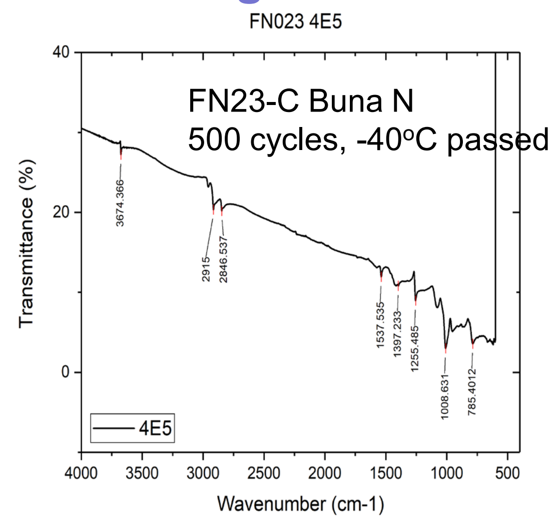
- **No significant increase in damage with increased number of cycles at -20°C.**
- **Damage increased with cycling at -40°C**
- **Effect of test temperature and the number of cycles is evident for these breakaways and the polymers within**

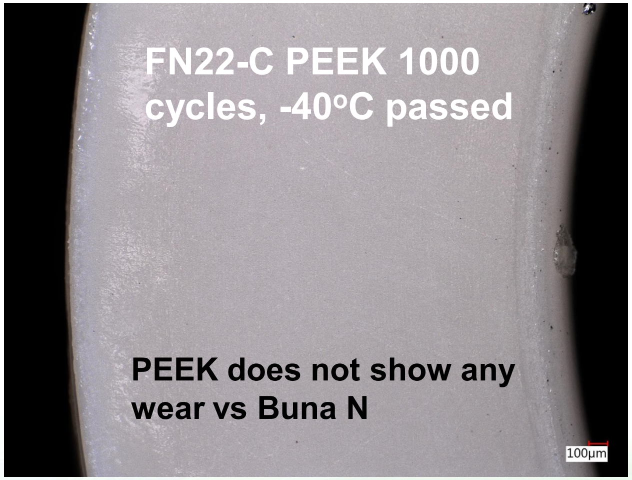
Accomplishment:
Polymer choice *critical* for performance in H_2

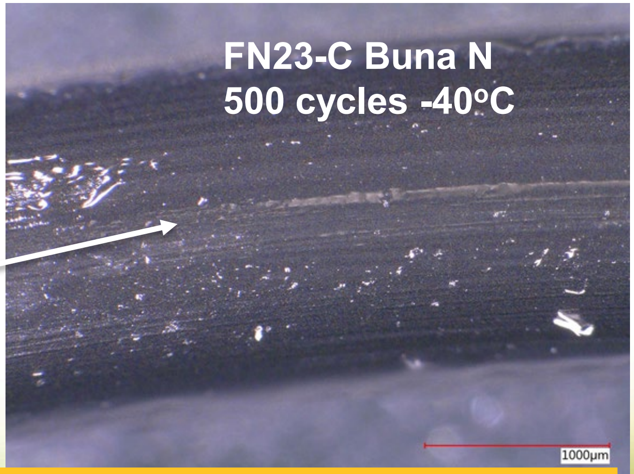
FTIR spectra and optical microscopy of polymers from fueling nozzle







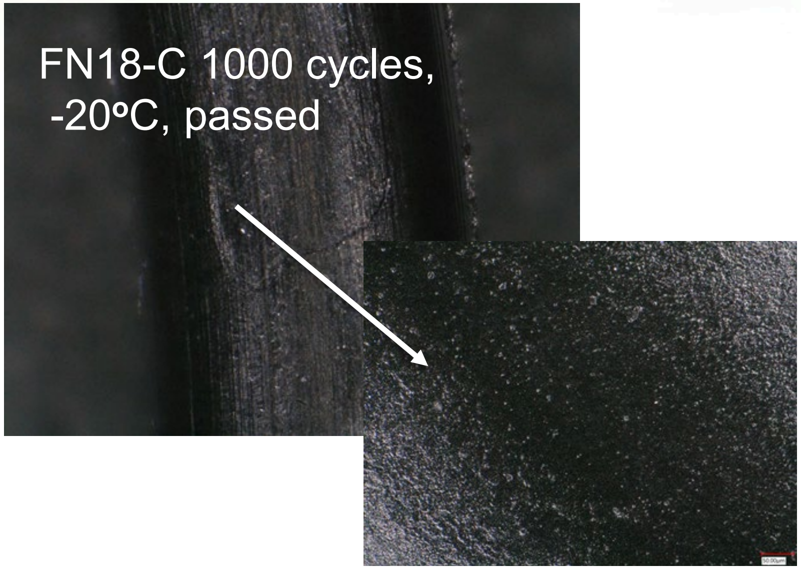


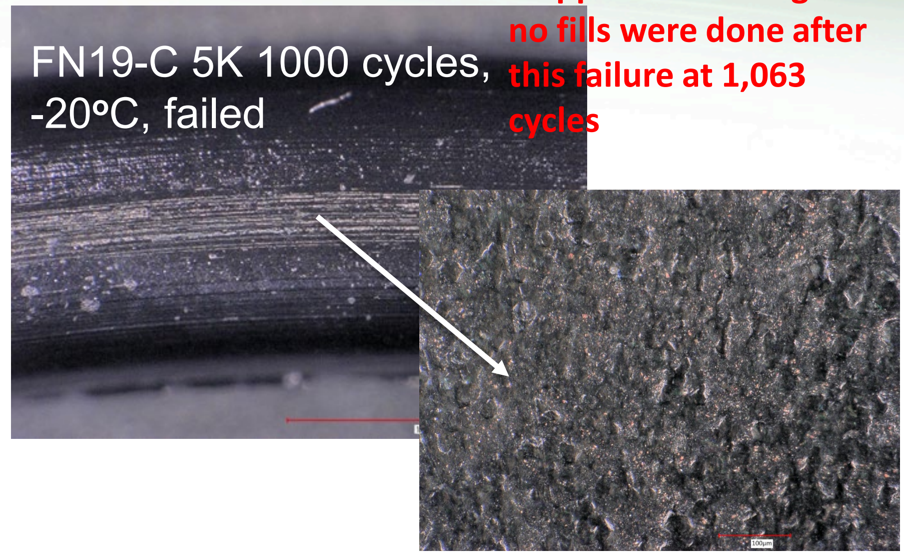


Increasing number of cycles at -40C shows increased wear in Buna N

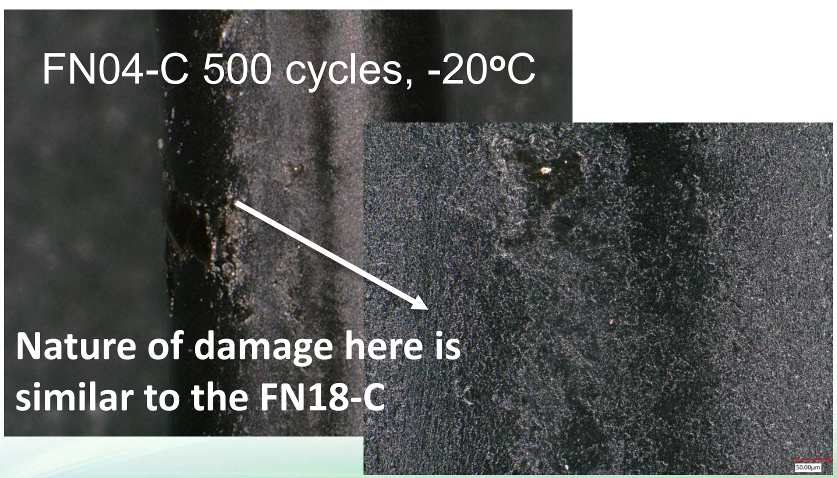
Accomplishment:

Extent of blistering and wear, leading to failure, can vary for the same component exposed to the same conditions





Leak from the nozzle stopped the testing and no fills were done after this failure at 1,063 cycles



- Two fueling nozzles tested at -20ºC from FN-C were compared for degradation modes (top row)
- Extent and nature of wear is different
- For FN19-C, extreme pitting and wear is seen with the Buna N rubber whereas with FN18-C had blisters
- FN19-C failed at 1000 cycles

Response to last year's Reviewer's comments

- This part of the project was not independently reviewed last year. See project in008 for reviewer responses.

Collaboration

SNL and NREL are using expertise at both labs with close coordination to execute this project

Component Manufacturers

- Team maintained an open communication with the breakaway/nozzle manufacturers as results became available

- NREL and SNL secured NDAs with both manufacturers and allowed them to review failure results + material analysis

Remaining Challenges and Future Work:

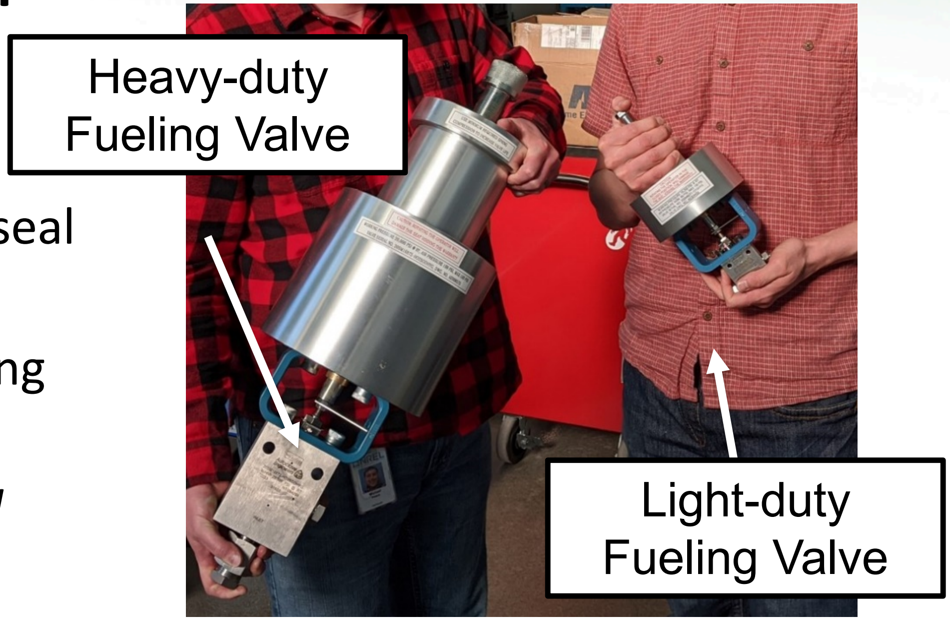
Publish findings and NREL findings (see in008) in a comprehensive final report

Move Towards the Future

- Develop novel polymeric materials or seal designs
- Develop additional work scope including coordination with H-MAT consortium

Coordinate additional testing at NREL and analysis at SNL with:

- Heavy-duty components (higher flows)
- Additional components and/or new component designs
- Higher cycle counts
- Increased thermal shock



Any proposed future work is subject to change based on funding levels.

Summary Slide

- Right choice of polymers make all the difference in mitigating failure
  - Chemistry of polymers play a role in resistance to hydrogen cycling
  - e.g. Buna N and PTFE showed more damage compared to PUR and PEEK
- Degradation modes examined in components indicate mostly physical damage to the polymeric O-rings; no evidence of chemical changes for test conditions
  - Tested PTFE showed physical fraying and cracks whereas in Buna N, wear, blisters and pitting was observed
- Damage in fueling nozzles and breakaways increased from 500 to 1000 cycles at -40C for Buna N rubber
- Degradation or the extent of damage did not increase with cycling for -20C testing
- The nature and the extent of the degradation was much less at -20C as compared to -40 components
- More component testing with >>1000 cycles at -40C can help inform both degradation and statistical analyses in the future