SAND2019-11216PE

Compatibility of polymers in hydrogen environments: Brief update on 2019 work

Presentation to Kyushu University team @ PNNL
July 23, 2019

H-Mat[SM] Hydrogen Materials Compatibility Consortium

PRESENTED BY

Nalini Menon, April Nissen, Jeff Campbell, Bernice Mills, Heidy Vega

Sandia National Laboratories, CA

*Sandia National Laboratories is a multi mission laboratory managed and operated by National Technology and Engineering Solutions of Sandia, LLC., a wholly owned subsidiary of Honeywell International, Inc., for the U.S. Department of Energy National Nuclear Security Administration under contract DE-NA0003525.

SAND2019-8603 PE

Sandia National Laboratories is a multimission laboratory managed and operated by National Technology & Engineering Solutions of Sandia, LLC, a wholly owned subsidiary of Honeywell International Inc., for the U.S. Department of Energy's National Nuclear Security Administration under contract DE-NA0003525.

Polymers in hydrogen environments: Challenges

1 Enable full deployment of H2 and Fuel Cell technologies
(STANDARD TEST PROTOCCOLS FOR POLYMER COMPATIBILITY IN HYDROGEN)

2 CRITICAL GAPS IN KNOWLEDGE BASE
(Degradation mechanisms, transport properties, friction and wear, fracture and fatigue)

3 MANY VARIABLES
(Polymers, components, testing and operating conditions)

COTS composition is unknown

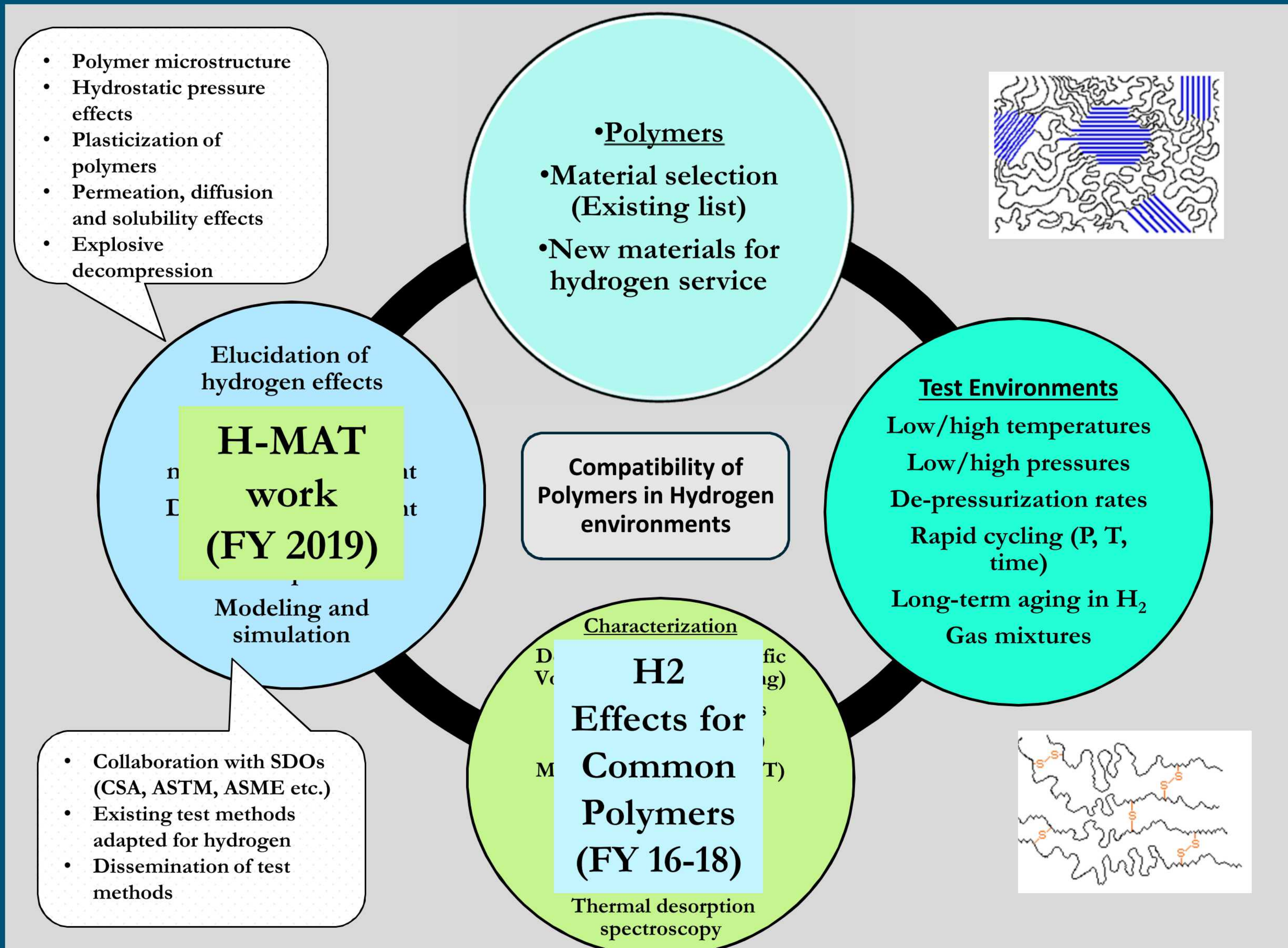
4 SUPPLIER-BASED DIFFERENCES
(Polymers, components)

5 Polymer Compositions
(additives)

Kyushu University/Takaishi Industry Collaboration

Mechanism of H2 effects

Strategy for Polymer compatibility with hydrogen



EFFECT OF FILLERS AND PLASTICIZERS ON POLYMERS IN H2

Elastomers: NBR (Nitrile butadiene rubber)

Takaishi Industry supplied 3 mm-thick 6” x 6” sheets of custom formulations (below)

	PNNL ref.#					
ITEMS	PNNL#N1	PNNL#N2	PNNL#N3	PNNL#N4	PNNL#N5	PNNL#N6
Features	No Filler No Plasticizer	No Filler Plasticizer	Carbonblack No Plasticizer	Inorganic No Plasticizer	Carbonblack Inorganic Plasticizer	Carbonblack Inorganic No Plasticizer
Our ref.#	NBR#1	NBR#101	NBR#3	NBR#5	NBR#100	NBR#63
NBR(Nipol 1042*)	100	100	100	100	100	100
Stearic Acid	1	1	1	1	1	1
Zinc Oxide	5	5	5	5	5	5
Sulfur	1.5	1.5	1.5	1.5	1.5	1.5
MBTS	1.5	1.5	1.5	1.5	1.5	1.5
TMTD	0.5	0.5	0.5	0.5	0.5	0.5
ZnEDC	-	-	-	-	-	-
DOS	-	10	-	-	10	-
Carbonblack(N330)	-	-	25	-	23**	19**
Silica(Nipsil VN3)	-	-	-	30	28**	23**
Density	1.032	1.015	1.118	1.152	1.182	1.175
Hardness (IRHD)	51.0	43.4	66.0	66.1	65.8	68.7

EFFECT OF FILLERS AND PLASTICIZERS ON POLYMERS IN H2

Elastomers: EPDM (Ethylene Propylene Diene monomer rubber)

Takaishi Industry supplied 3 mm-thick 6” x 6” sheets of custom formulations (below)

	PNNL ref.#					
ITEMS	**PNNL#E1**	**PNNL#E2**	**PNNL#E3**	**PNNL#E4**	**PNNL#E5**	**PNNL#E6**
Features	No Filler No Plasticizer	No Filler Plasticizer	Carbonblack No Plasticizer	Inorganic No Plasticizer	Carbonblack Inorganic Plasticizer	Carbonblack Inorganic No Plasticizer
Our ref.#	EPDM#1	EPDM#101	EPDM#3	EPDM#5	EPDM#100	EPDM#29
EPDM(Esprene505*)	100	100	100	100	100	100
Stearic Acid	1	1	1	1	1	1
Zinc Oxide	5	5	5	5	5	5
Sulfur	1.5	1.5	1.5	1.5	1.5	1.5
MBTS	1.5	1.5	1.5	1.5	1.5	1.5
TMTD	0.7	0.7	0.7	0.7	0.7	0.7
ZnEDC	0.7	0.7	0.7	0.7	0.7	0.7
DOS	-	10	-	-	10	-
Carbonblack(N330)	-	-	25	-	21**	16**
Silica(Nipsil VN3)	-	-	-	30	25**	20**
Density	0.921	0.919	1.013	1.039	1.073	1.053
Hardness (IRHD)	55.3	48.3	67.2	76.3	72.0	71.9

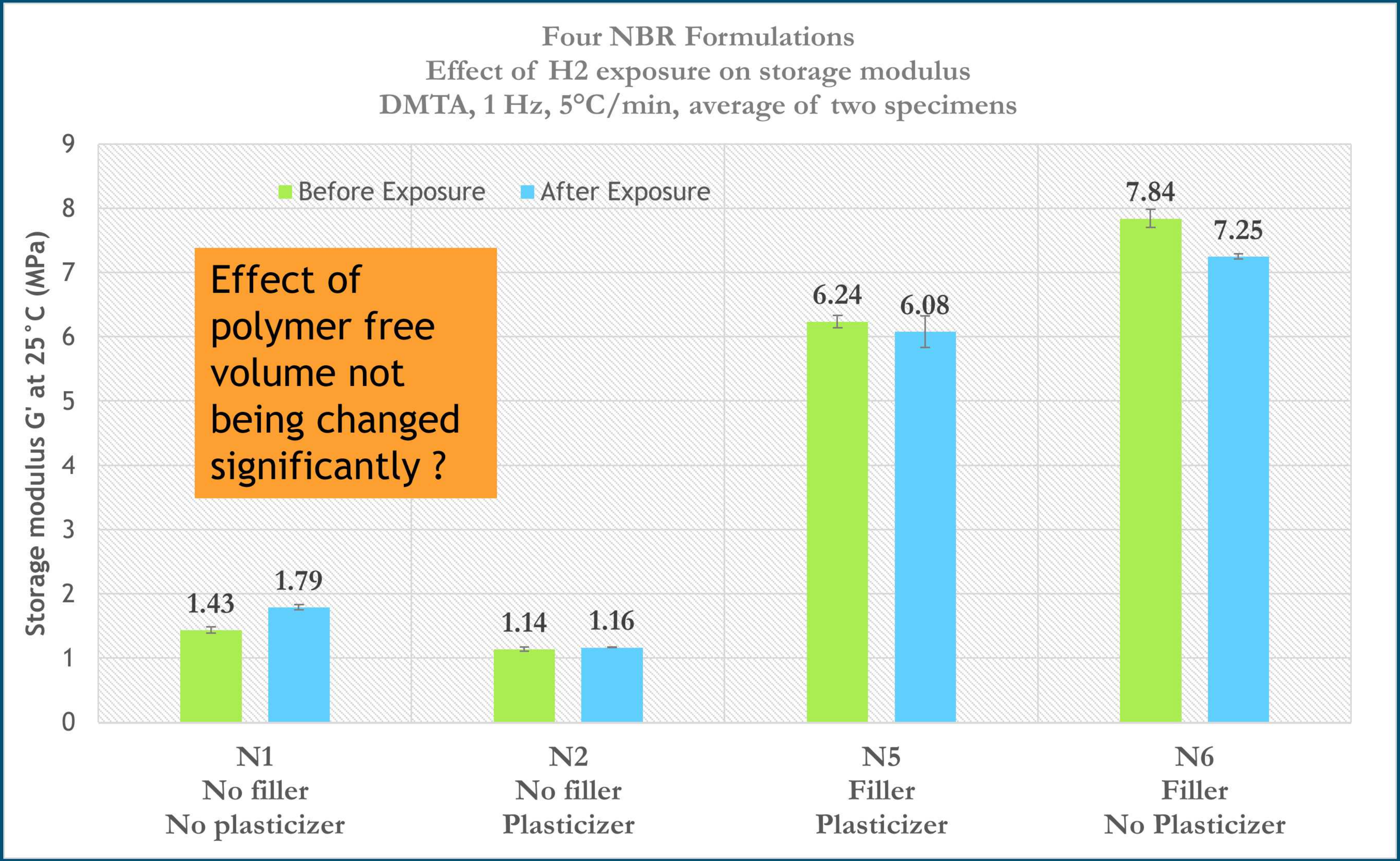
Linking H2 effects to polymer micro structure

1. Conditions of exposure: static high pressure (100 MPa) @ ambient temperature vs. cycling between 12 and 86 MPa at ambient temperature
2. Polymer interaction: free volume, crosslinking, polar grps
3. Filler and plasticizers: H2 retention by adsorption

Can property changes be due to interactions at different length scales?

1. Storage modulus – macro effect; bulk property
2. Compression set – Lower length scales ??
3. Density – macro effect ??
4. – lower length scales??

Hydrogen effects in Nitrile Rubber from fillers and additives: Storage modulus (Static test)



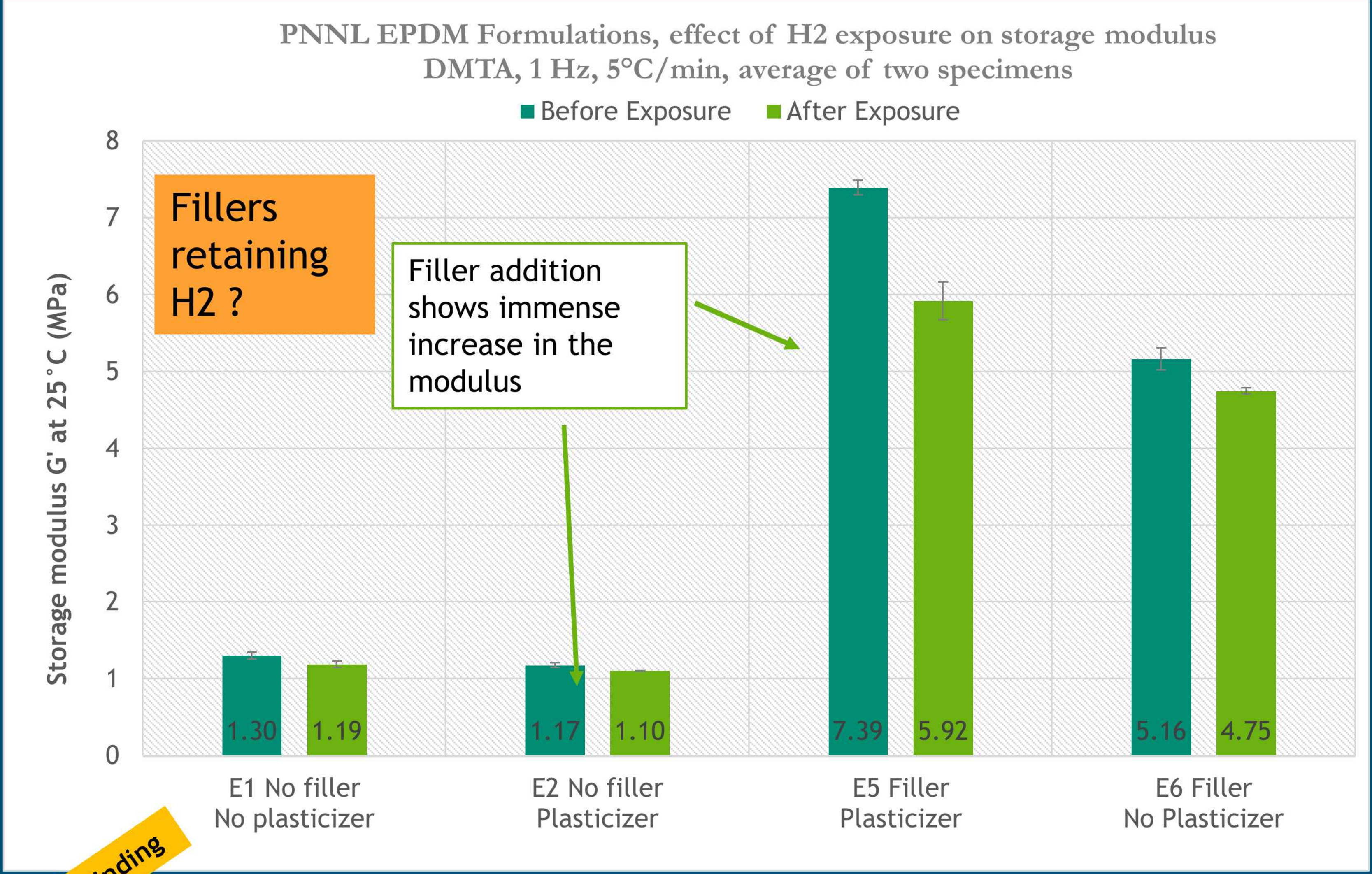
Modulus decrease due to H2 exposure for filled plasticized NBR is insignificant:
Change is not significant or permanent for one cycle of exposure on macro scale

MNC

Slide 7

MNC2 Menon, Nalini Chulliyil, 9/16/2019

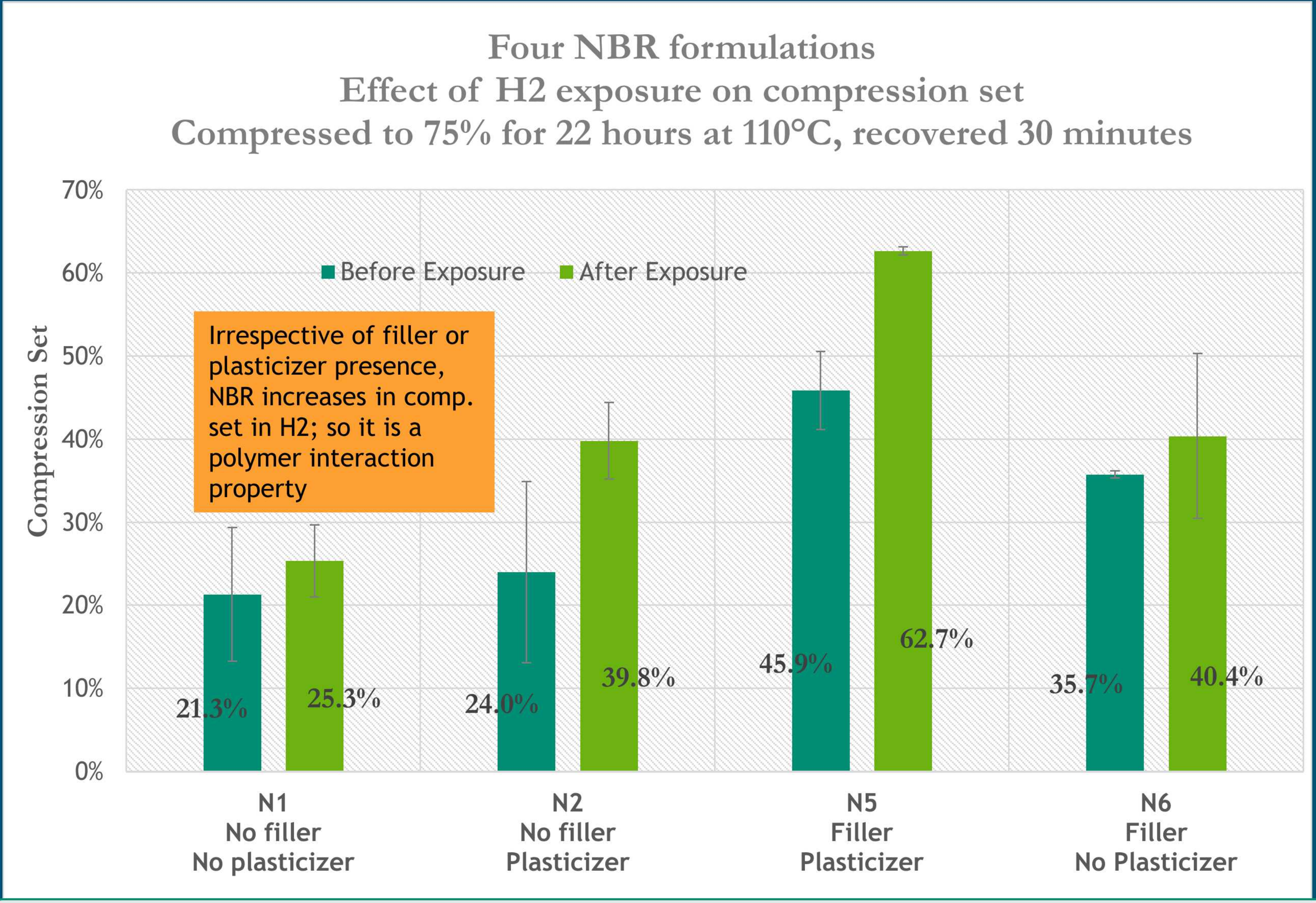
Hydrogen effects in EPDM from fillers and additives: Storage modulus (Static test)



New finding

A 20% decrease in modulus is seen in filled plasticized EPDM after once cycle of H2 exposure – significant macro change, plasticization of EPDM with H2; permanent effect

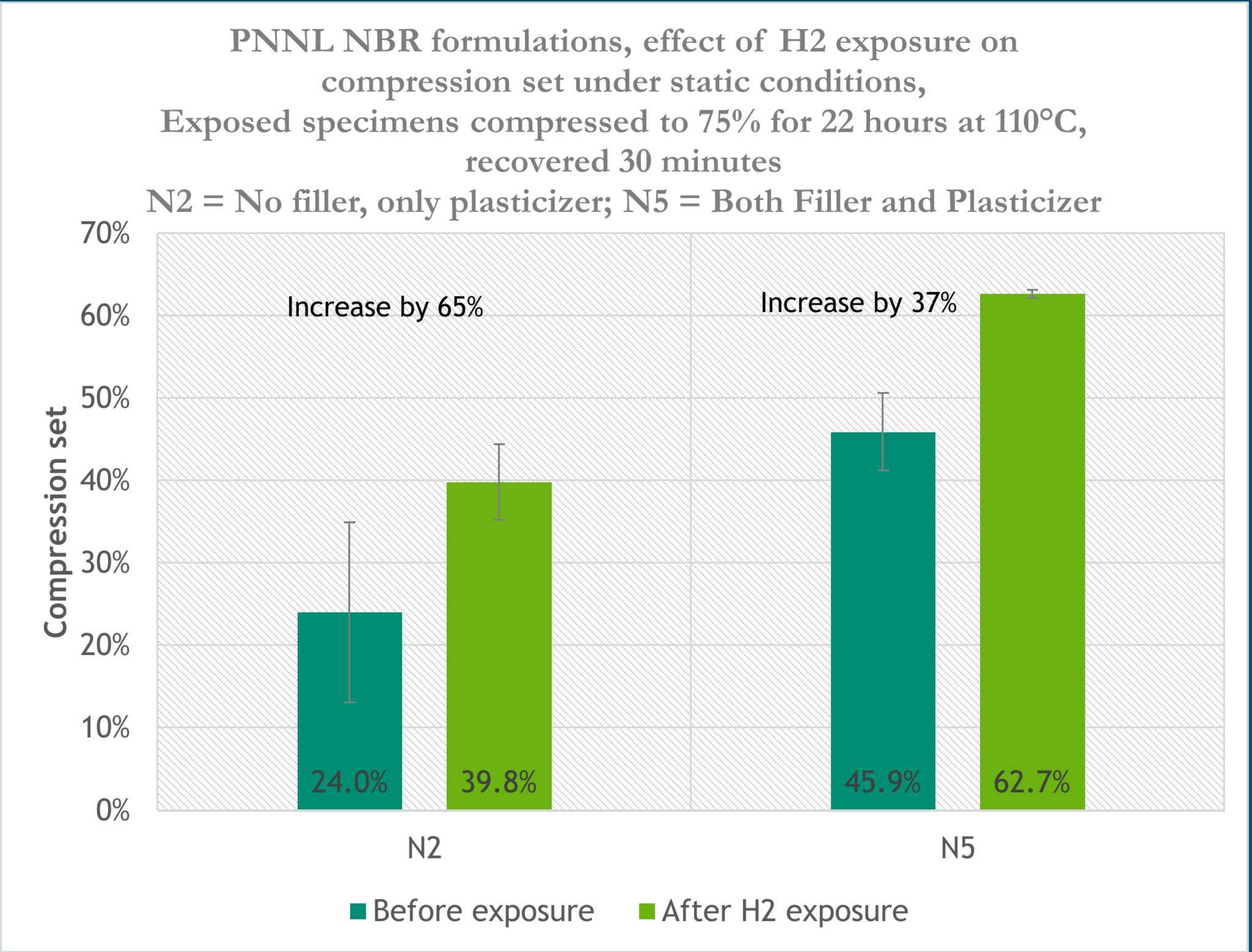
Hydrogen effects in Nitrile Rubber from fillers and additives: Compression set (Static test)



Compression set increased by ~37% due to H_2 exposure for a filled plasticized NBR system: Significant and permanent effect on lower length scale, extent depends on filler/plasticizer presence

MNC1

Taking a closer look: Effect of fillers and plasticizers in NBR (Static test)

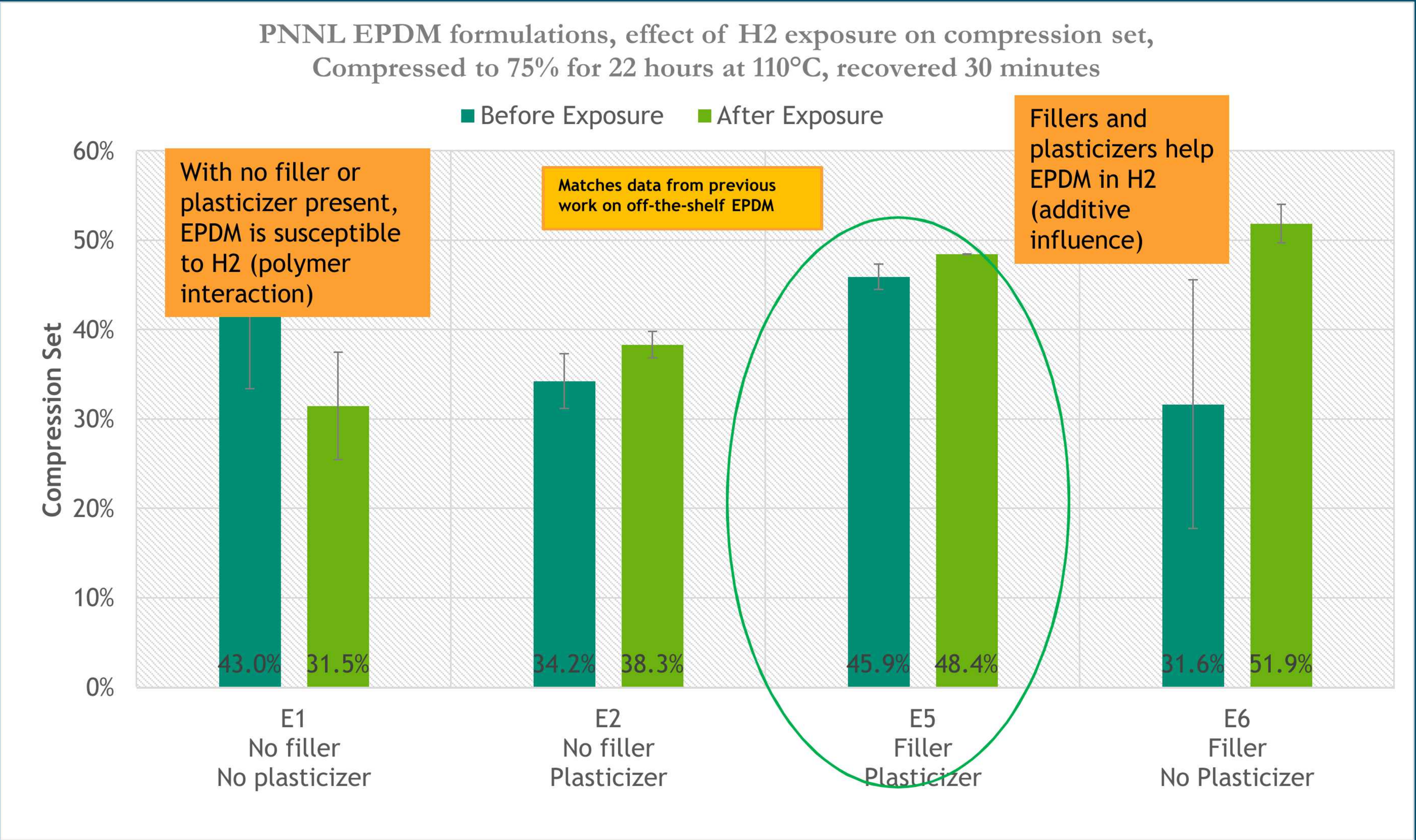


Plasticizers increase compression set (65% increase) and fillers mitigate compression set (decreased to 37%); also seen as crack mitigation when examined using micro CT

Slide 10

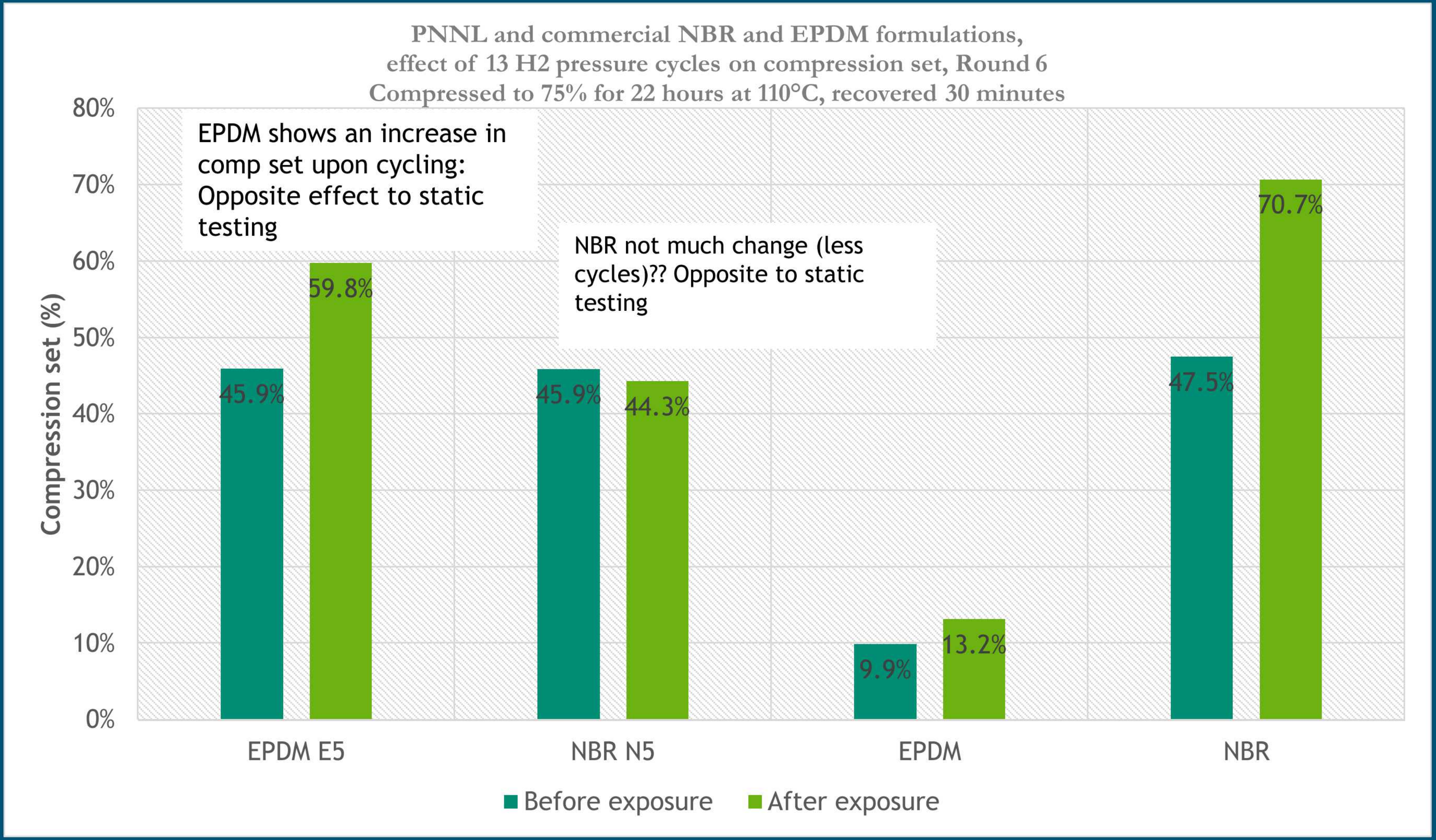
MNC1 Menon, Nalini Chulliyil, 7/22/2019

Hydrogen effects in EPDM from fillers and plasticizers: Compression set (Static test)

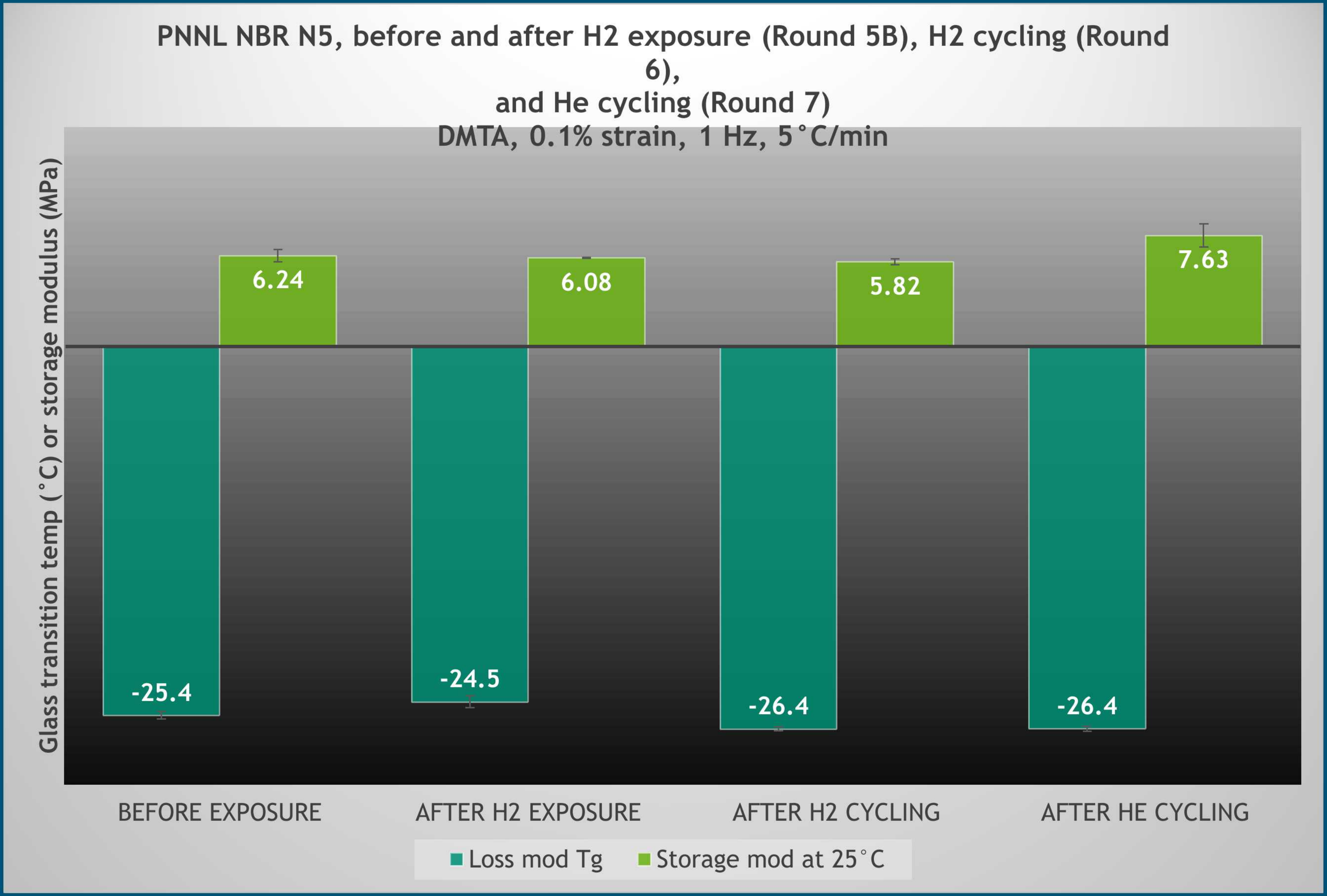


Compression set change due to H2 exposure for a filled, plasticized EPDM system is insignificant: lower free volume and high crosslink density, less effect of filler and plasticizer than NBR

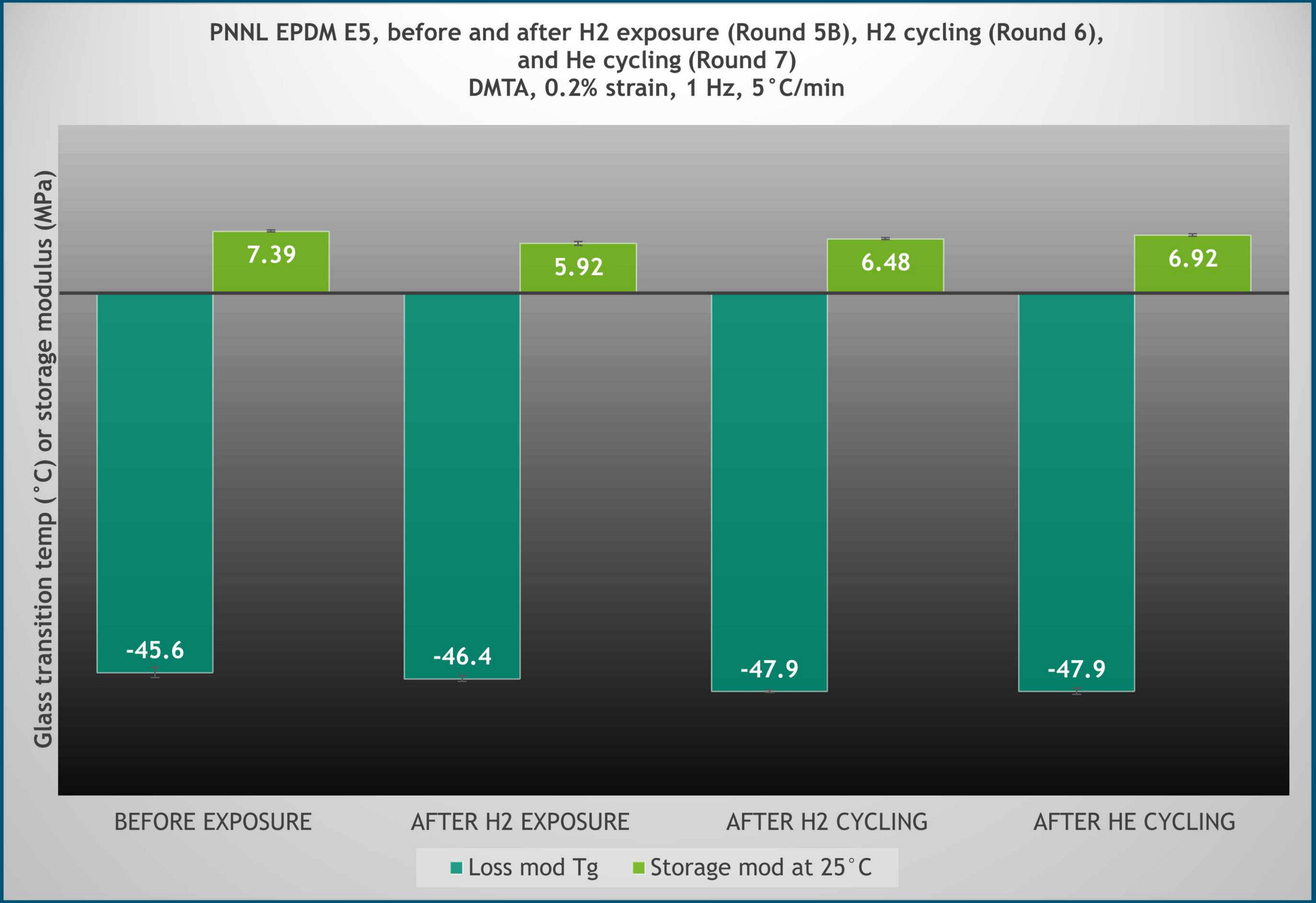
Hydrogen effects in EPDM from fillers and plasticizers: Compression set (Cycling test)



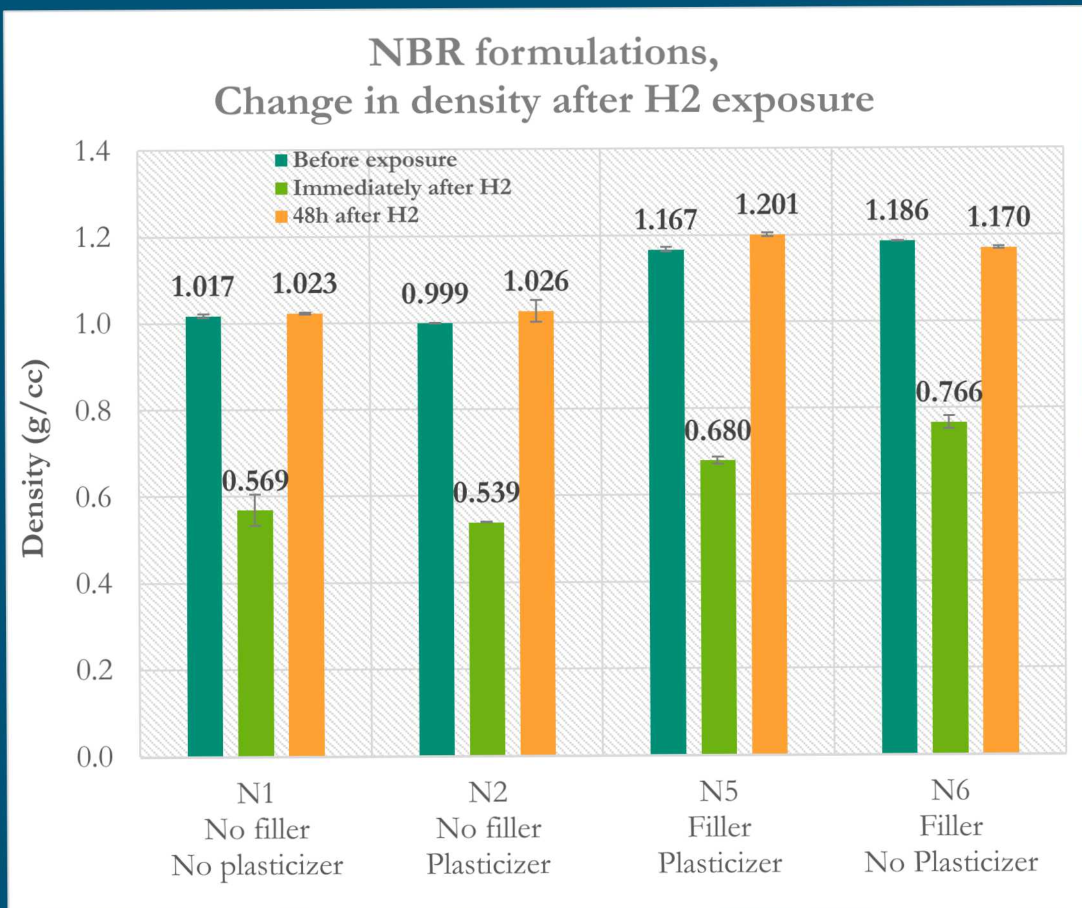
Hydrogen effects in Nitrile Rubber from fillers and additives: DMTA (Static and Cycling test)



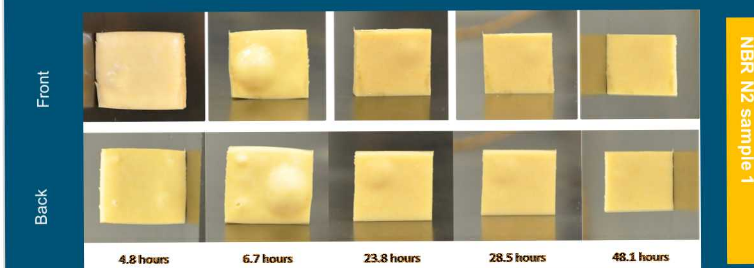
Hydrogen effects in EPDM from fillers and additives: DMTA (Static and Cycling test)

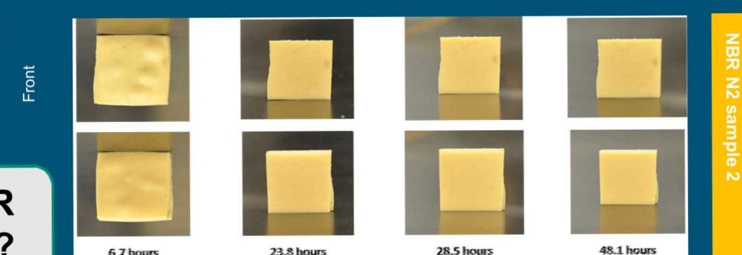


Hydrogen effects in Nitrile Rubber from fillers and additives: Density (Static test)



#	Filler	Plasticizer	Percent increase in volume	Recovery in volume
N1	No	No	79%	99%
N2	No	Yes	85%	97%
N5	Yes	Yes	72%	97%
N6	Yes	No	55%	101%

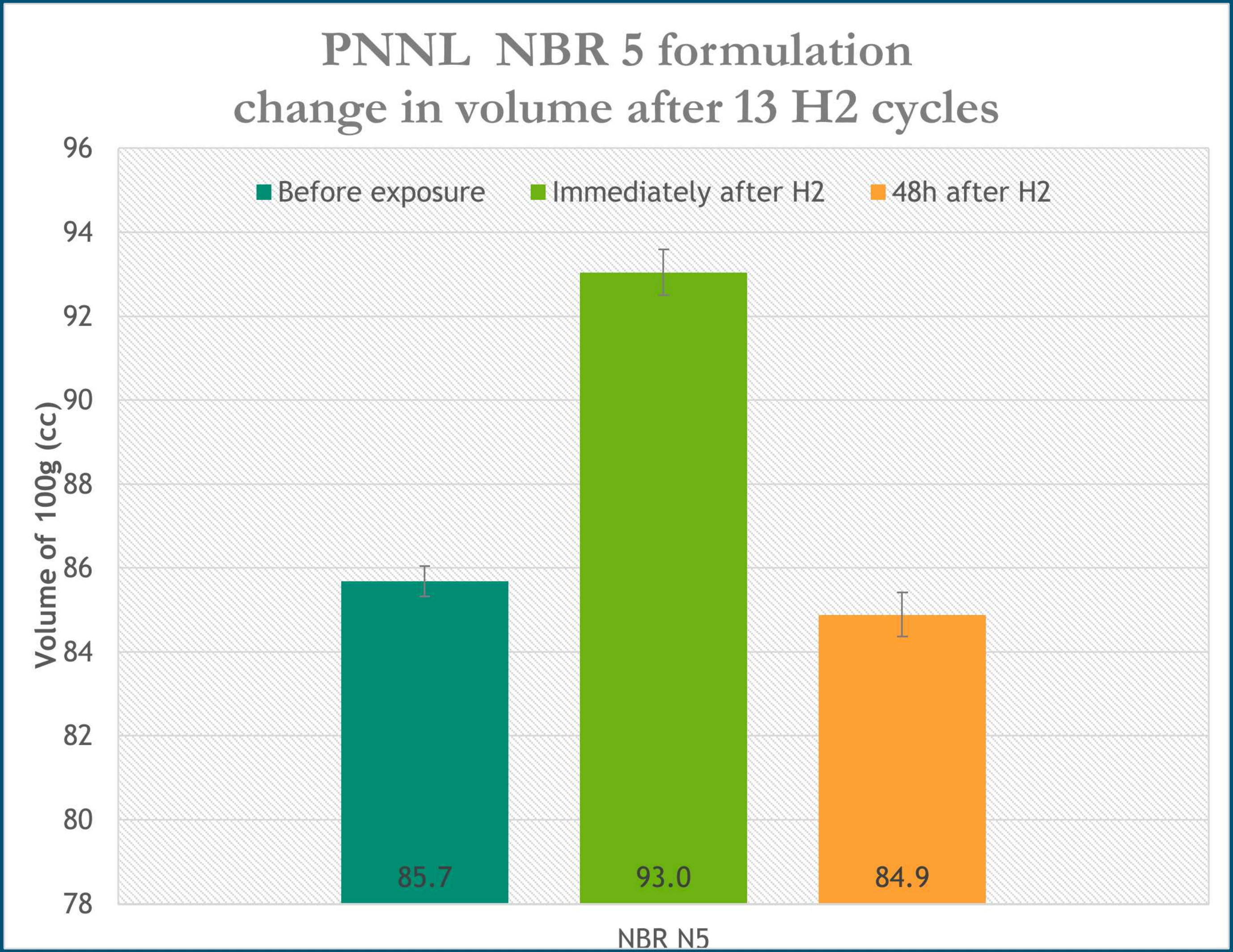




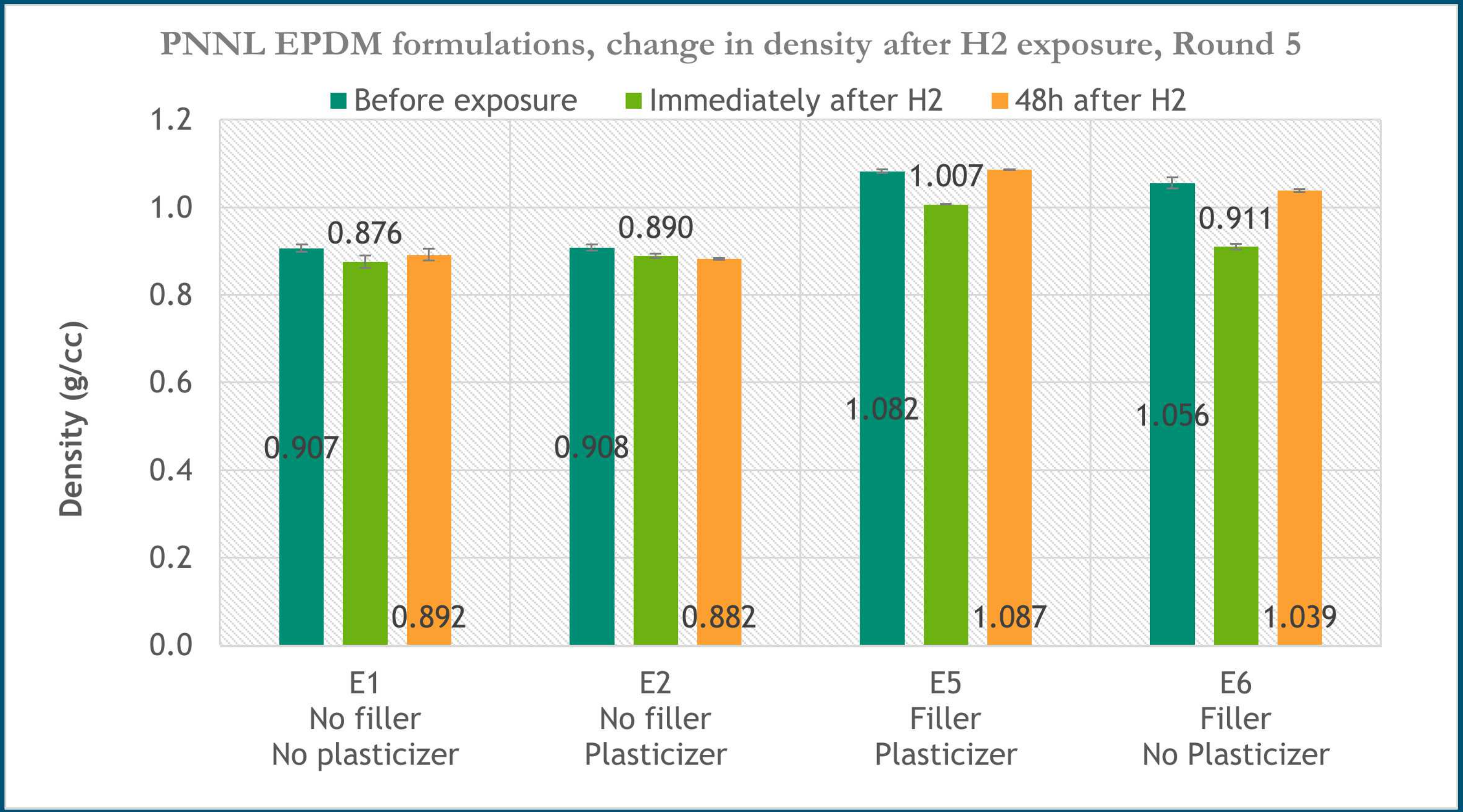
Picture showing the evolution of H2 from NBR N2 over 48 hours

Density changes due to H2 exposure for filled plasticized NBR (N5) is insignificant: non-permanent at a lower length scale ??

H2 Effects in NBR due to cycling



Hydrogen effects for EPDM with fillers and plasticizers : Density (Static test)

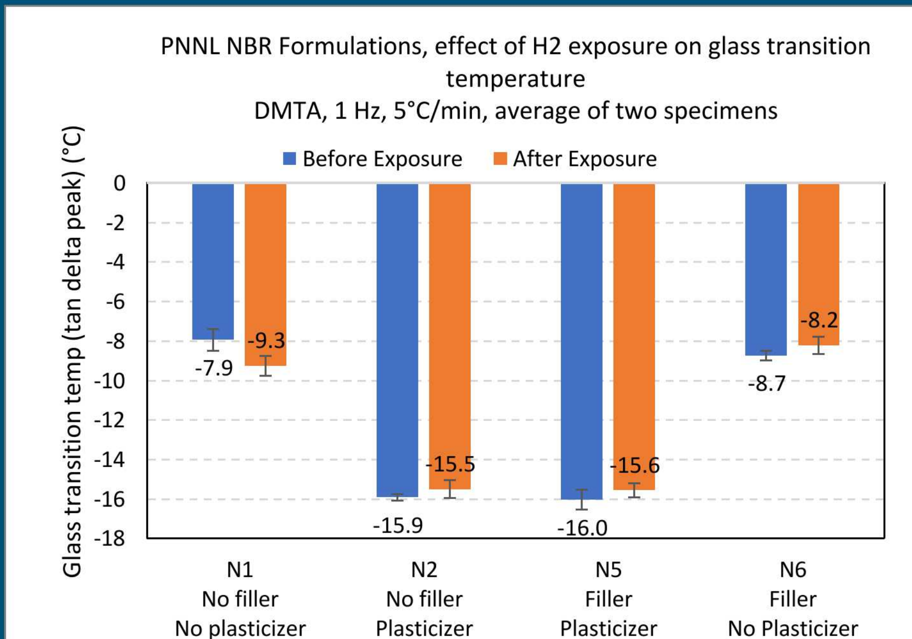


#	Filler	Plasticizer	Percent increase in volume	Recovery in volume
E1	No	No	4%	102%
E2	No	Yes	2%	103%
E5	Yes	Yes	8%	100%
E6	Yes	No	16%	102%

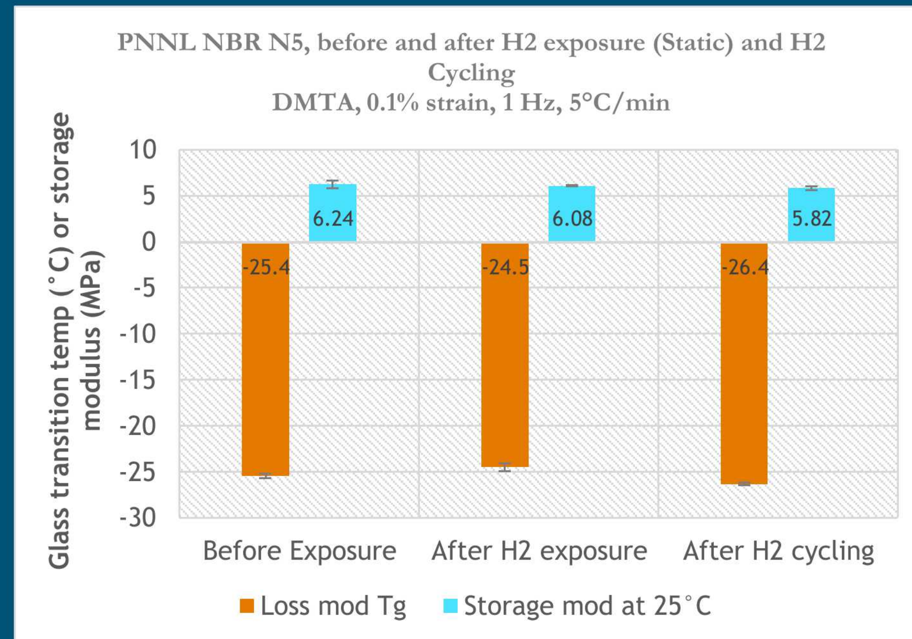
Density changes due to H2 exposure for filled plasticized EPDM is insignificant: non-permanent at a lower length scale ??

Glass transition temperature changes: NBR

Static Exposure



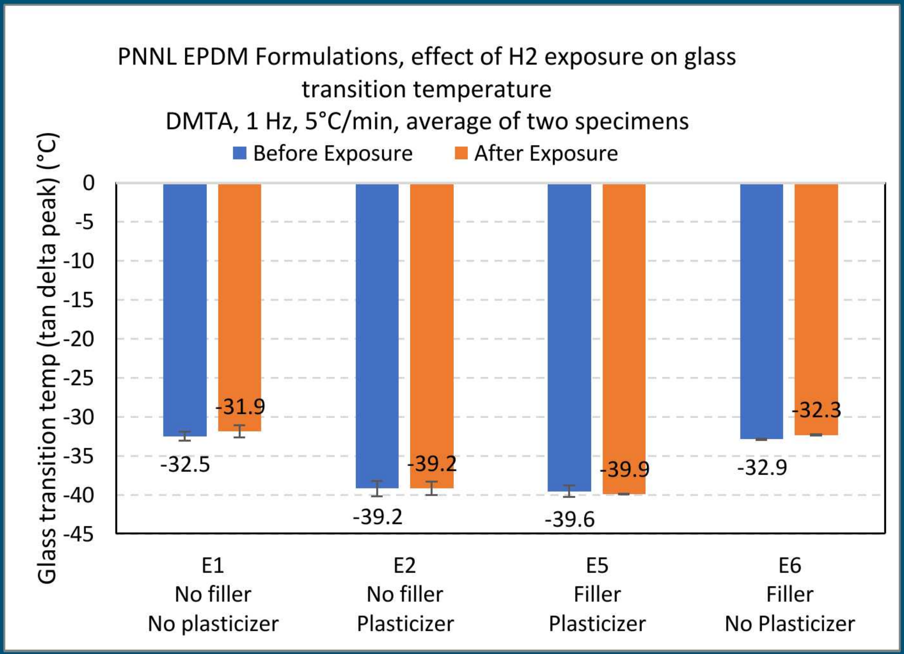
Static and Cycling Exposure

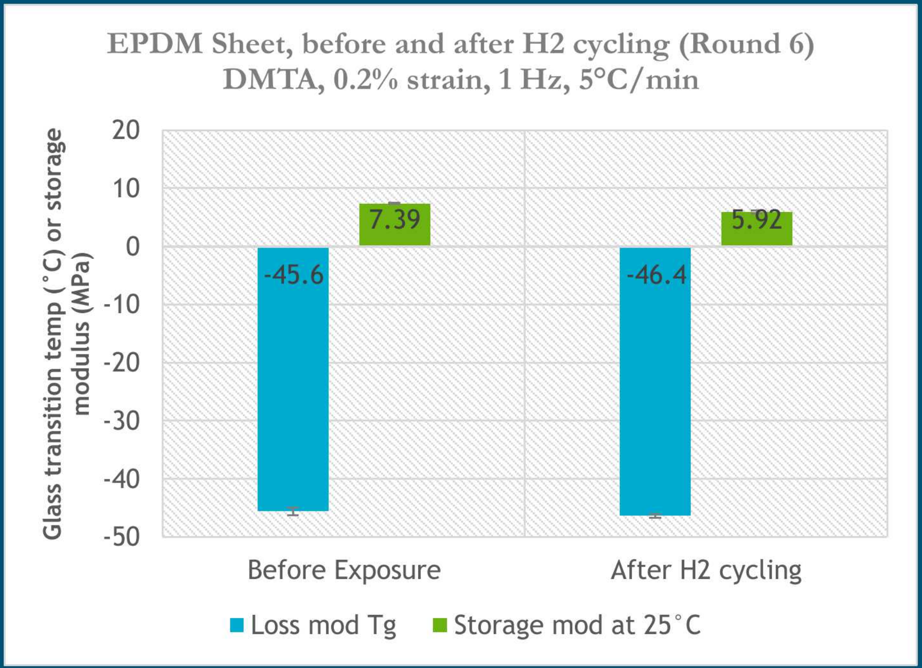


- Plasticizer addition decreases T_g significantly; whereas filler addition does not change it significantly
- For a filled plasticized NBR, static exposure did not change Tg significantly

For a filled, plasticized NBR system, cycling in H2 has started a decrease T_g and modulus

Glass transition temperature changes: EPDM





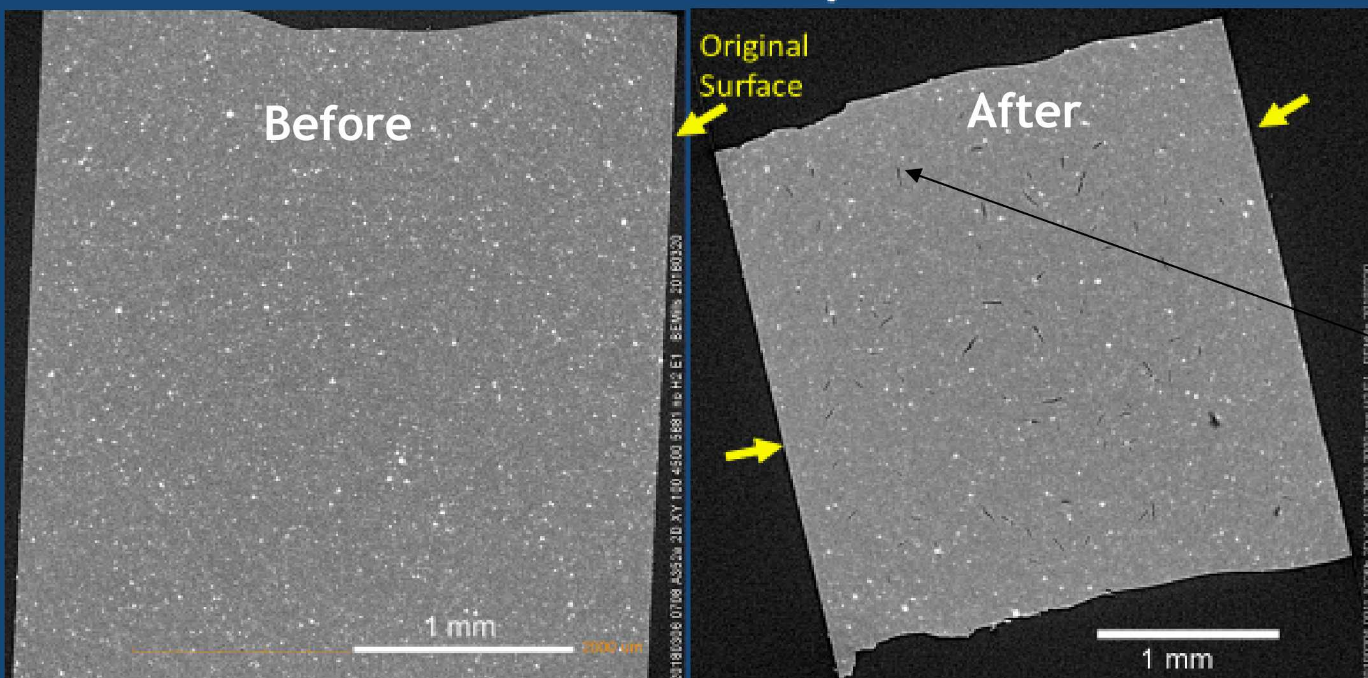
- **Plasticizer addition and filler addition does not change T_g significantly**
- **For a filled plasticized NBR, static exposure did not change Tg significantly**

For a filled, plasticized EPDM system, cycling in H2 has started a decrease T_g and modulus

Sandia National Laboratories

Micro-CT images for EPDM after H2 exposure

H2 exposure of EPDM E1 shows numerous slit-shaped voids.



There is no preferred orientation.

- Formulation EPDM E1 has no filler or plasticizer
- Both formulations contain high Z particles (5% by wt. ZnO)

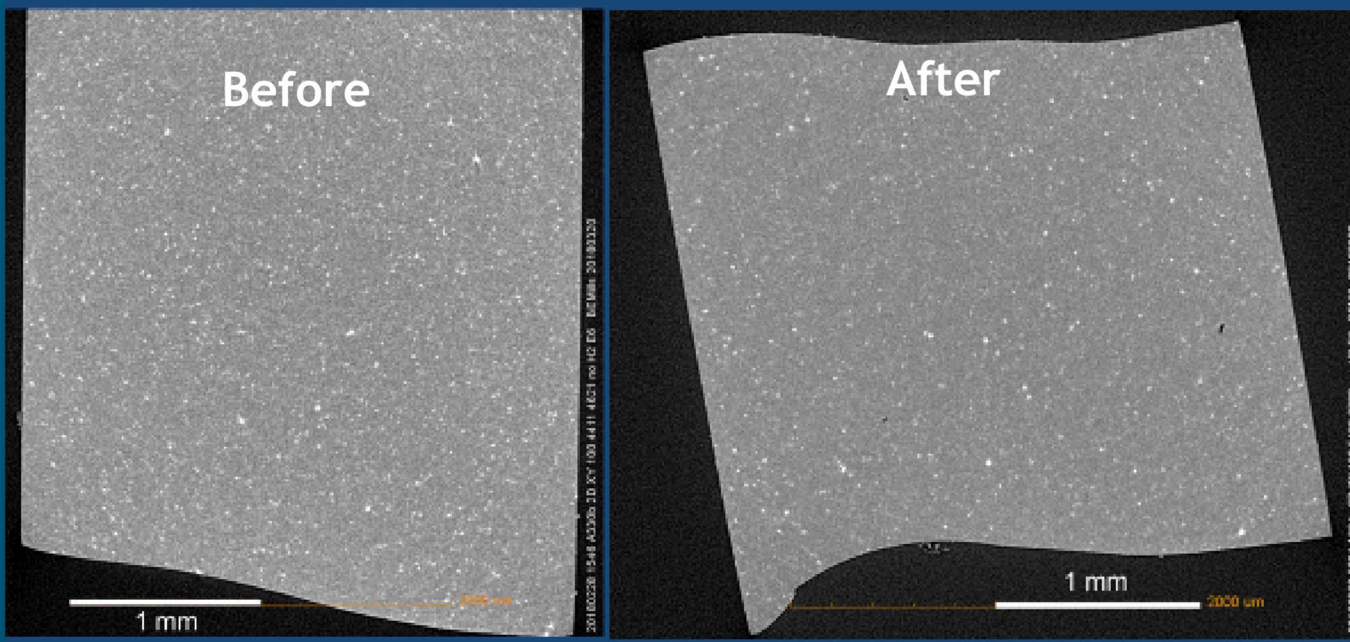
Microcracks in picture are not aligned in any particular direction and seem more or less distributed all over

Unfilled EPDM after H2 exposure has significant microcrack damage

Sandia National Laboratories

Micro-CT images for EPDM after H2 exposure

H2 exposure of EPDM E6 generates fewer but larger voids.



There is no preferred position within the sample.

- Formulation EPDM E6 has filler but no plasticizer
- Fillers in EPDM E6 are: carbon black (300 nm) and Silica
- Both formulations contain high Z particles (5% by wt. ZnO)

Fillers appear to help with crack mitigation in EPDM after H2 exposure

Sandia National Laboratories

EPDM compared

F P voids rare but some are large; most are very small. Large voids have serrated edges. Faint patches are probably agglomerations of fumed silica.

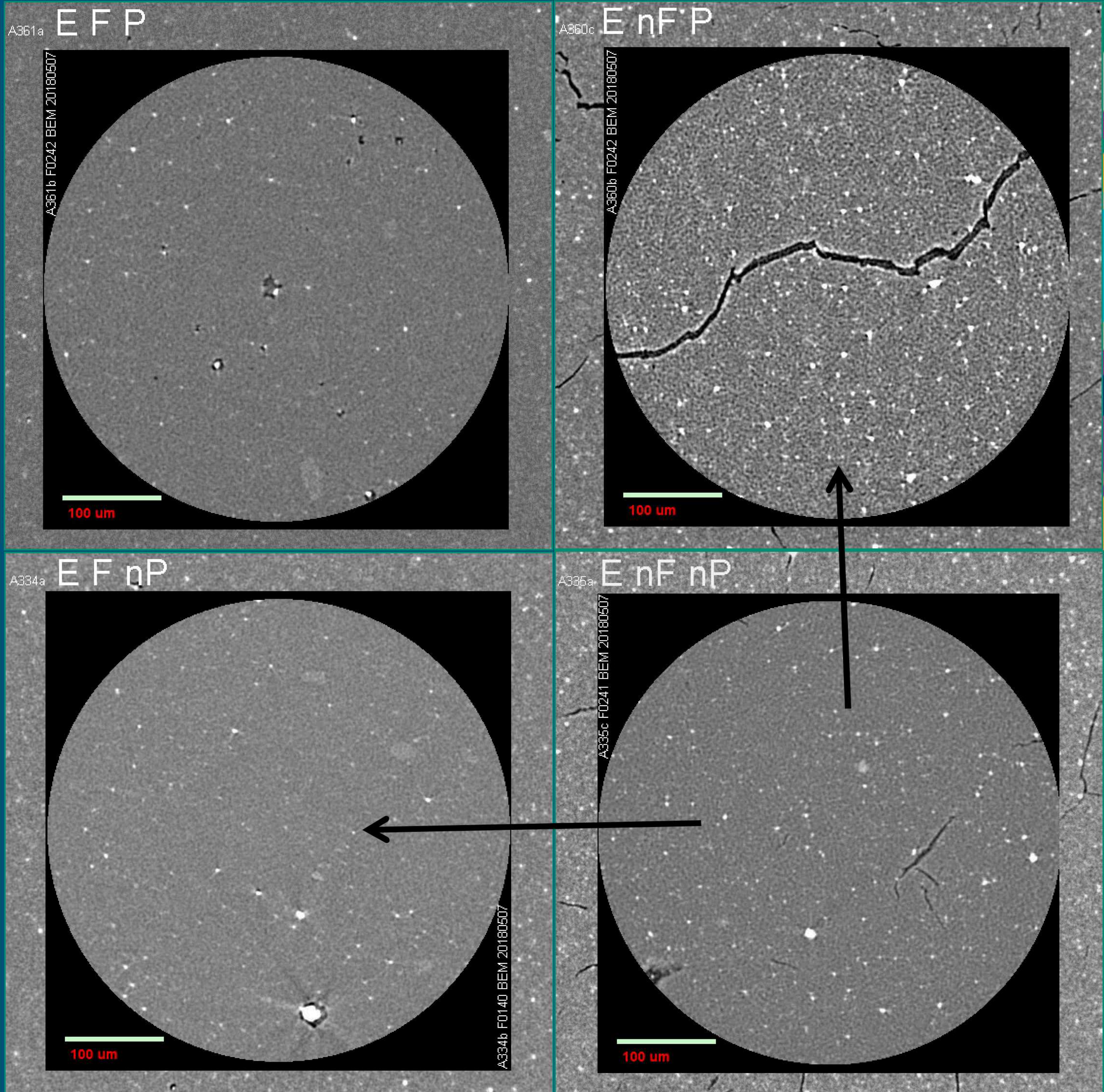
nF P worst case with long cracks.

F nP very few voids, small. Silica agglomerations indicate incomplete mixing.

nF nP a large number of medium sized cracks. Sample is friable (crumbles easily) even before hydrogen.

FP 2	P 4
F 1	3

1 Best > 4 Worst



EPDM compared

F P voids rare but some are large; most are very small. Closest to commercial formulation.

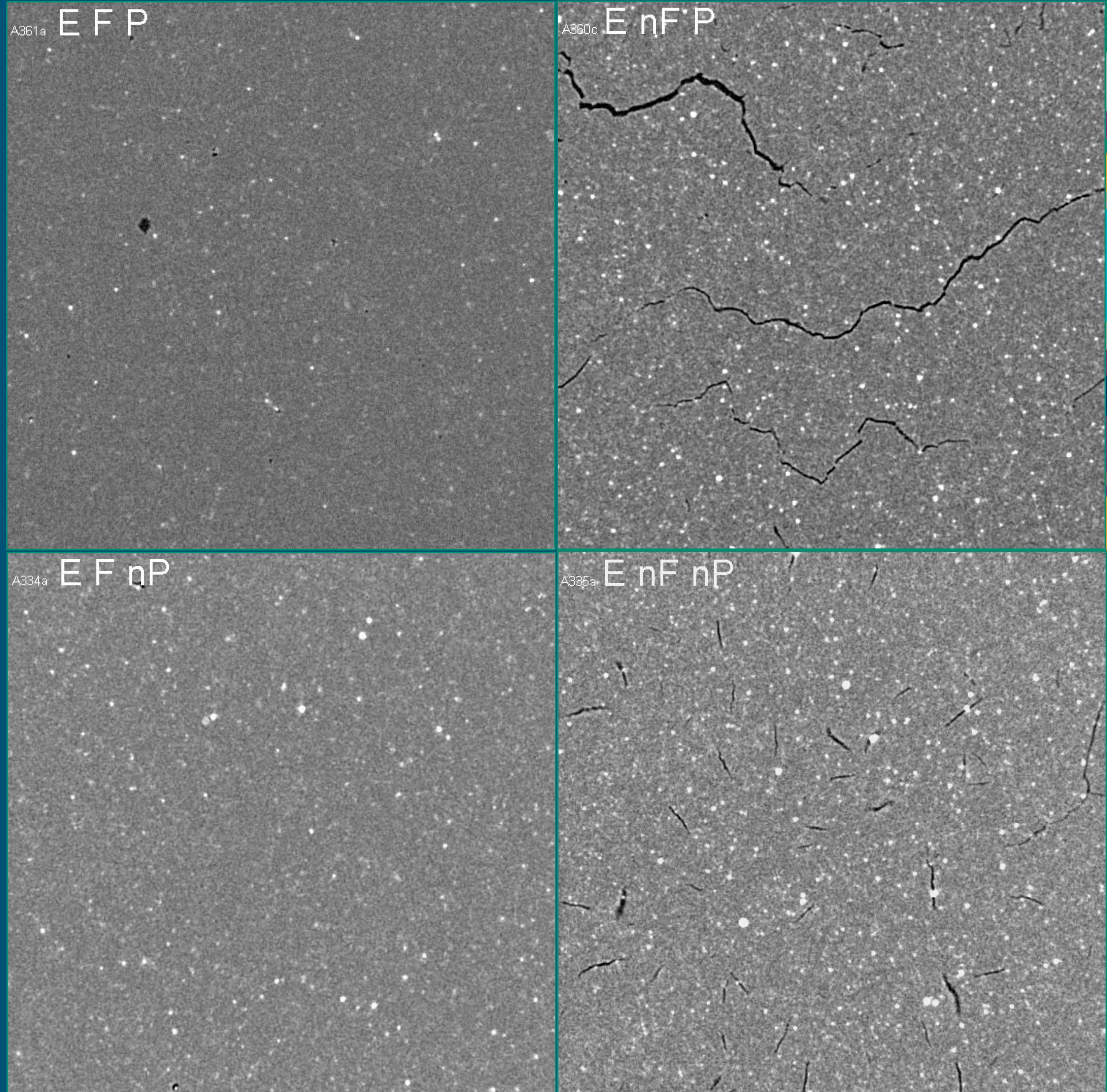
nF P worst case with long cracks.

F nP very few voids, small.

nF nP a large number of medium sized cracks. Sample is friable (crumbles easily) even before hydrogen exposure.

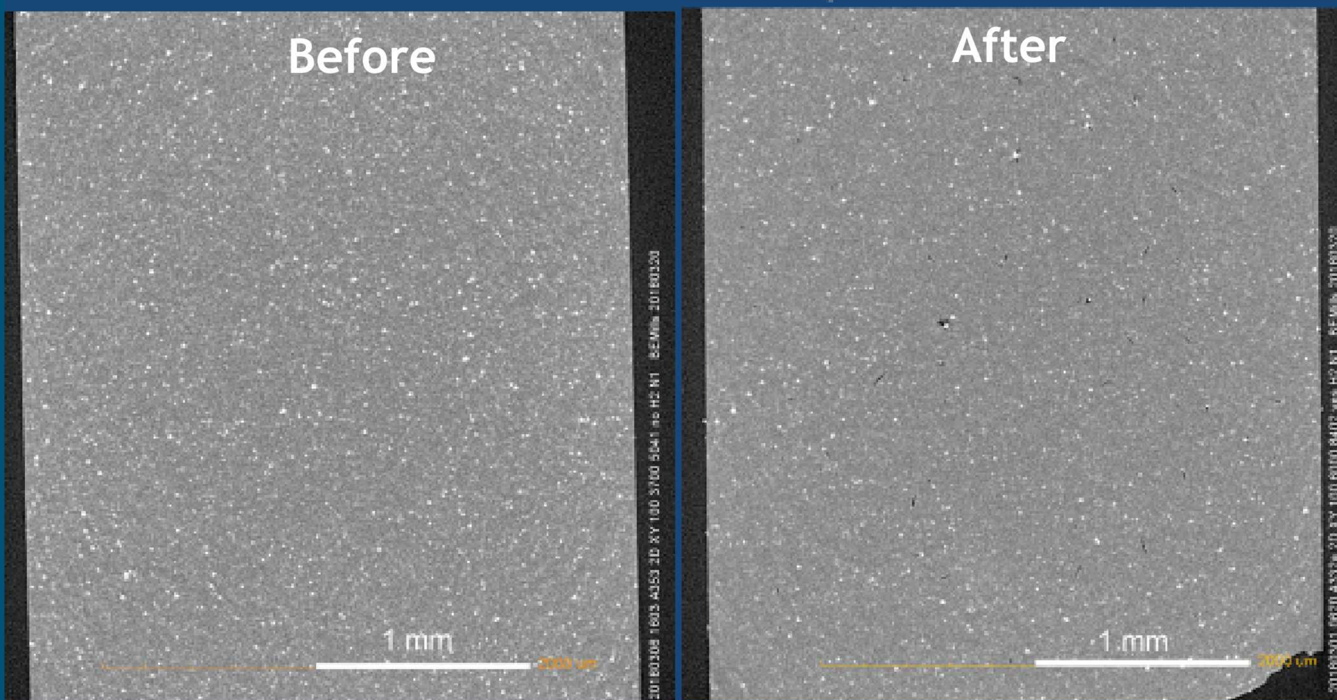
FP 2	P 4
F 1	3

1 Best > 4 Worst



Accomplishments and Progress
Micro-CT images for NBR after H2 exposure

H2 exposure of NBR N1 shows fewer and smaller slit-shaped voids.



There is no preferred orientation. There are perhaps a few more voids in the interior—need to confirm.

Comparison of EPDM and NBR before and after hydrogen exposure BEMills 20180320

- Formulation NBR N1 has no filler or plasticizer
- Both formulations contain high Z particles (5% by wt. ZnO)

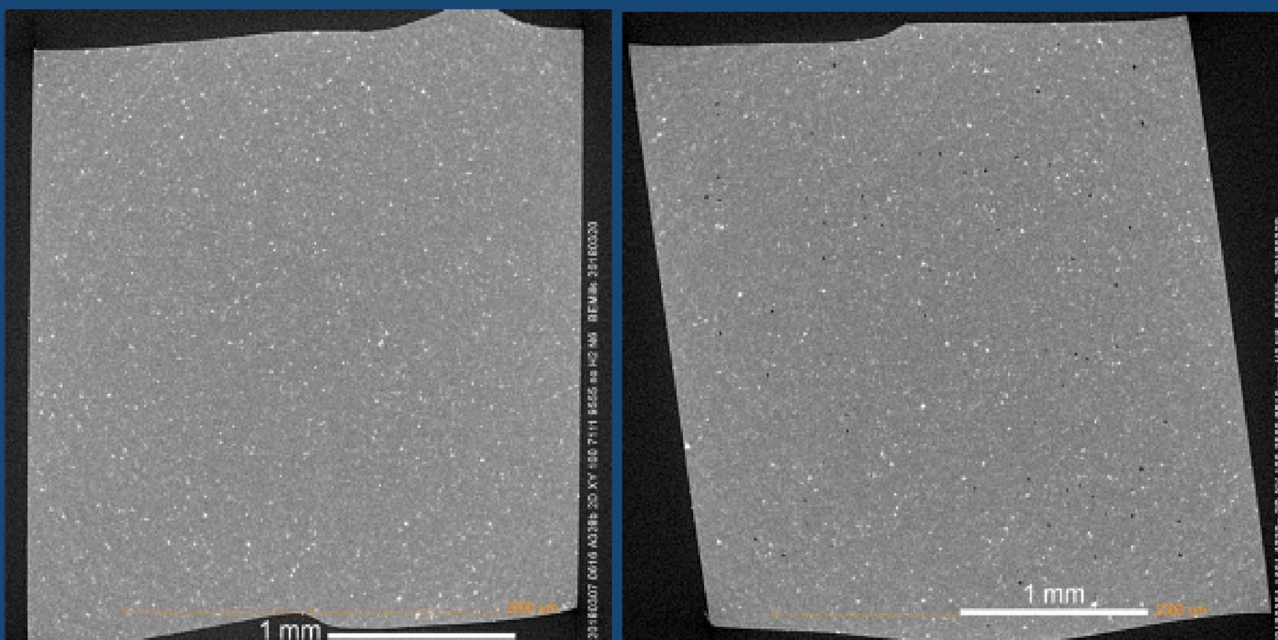
Microcracks in left picture changed to more pin-point voids in right picture which are not aligned in any particular direction and seem more or less distributed all over

Microcrack damage is less significant and more pin-point in shape

Sandia National Laboratories

Accomplishments and Progress
Micro-CT images for NBR after H_2 exposure

H_2 exposure of NBR N6 shows large numbers of small isotropic voids.



There is no preferred position within the sample.

Comparison of EPDM and NBR before and after hydrogen exposure BEMills 20180320

- Fillers in EPDM E6 are: carbon black (300 nm) and Silica
- Both formulations contain high Z particles (5% by wt. ZnO)

Fillers appear to change the nature of cracks/voids in NBR after H_2 exposure

Sandia National Laboratories

NBRs compared

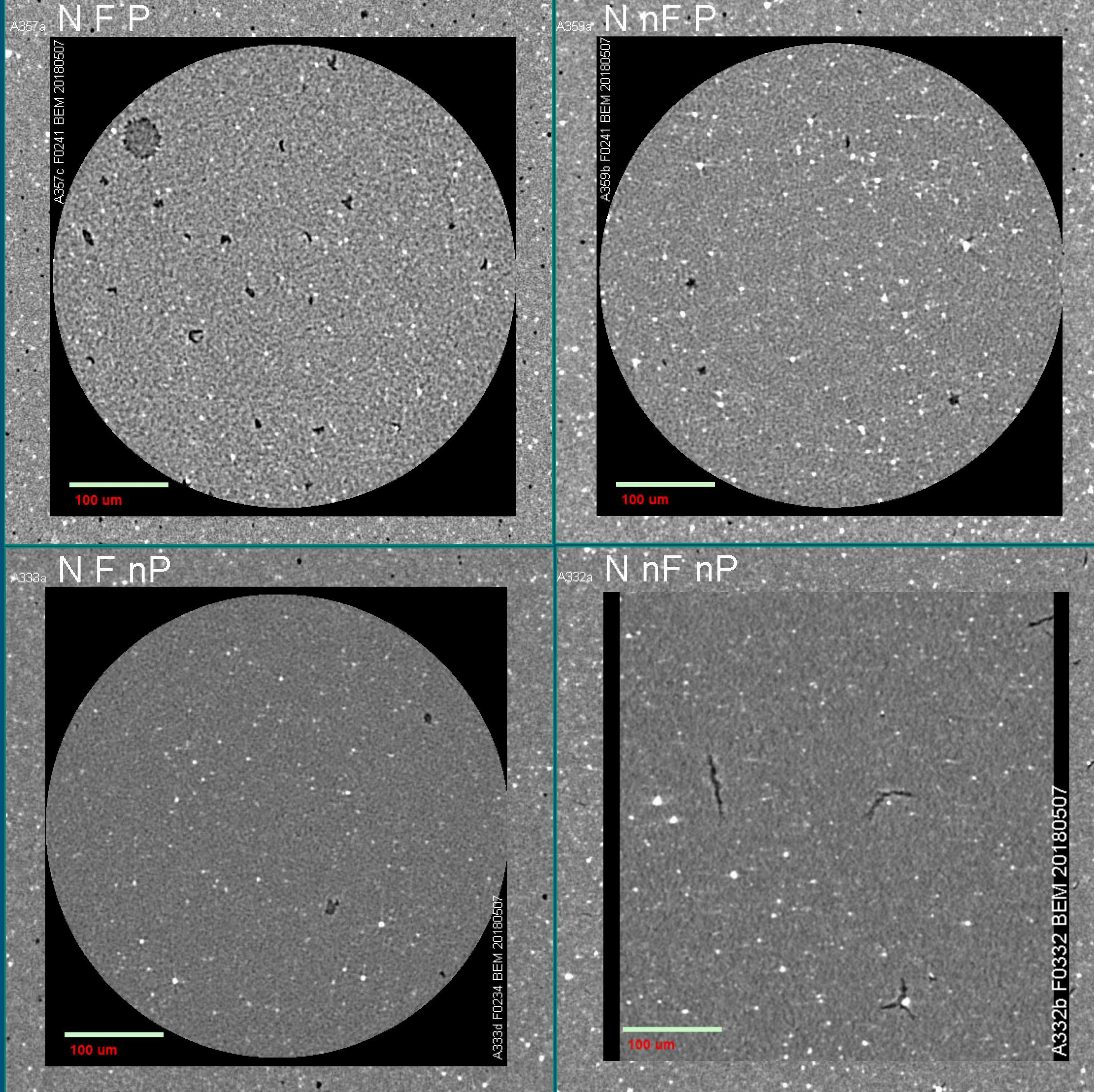
FP: many voids; some large voids have serrated edges. Closest to commercial formulation.

nF P: many small voids

F nP fewer voids; medium sized.

nF nP linear voids aka cracks

Filler addition helps in mitigating H2 effects



NBRs compared

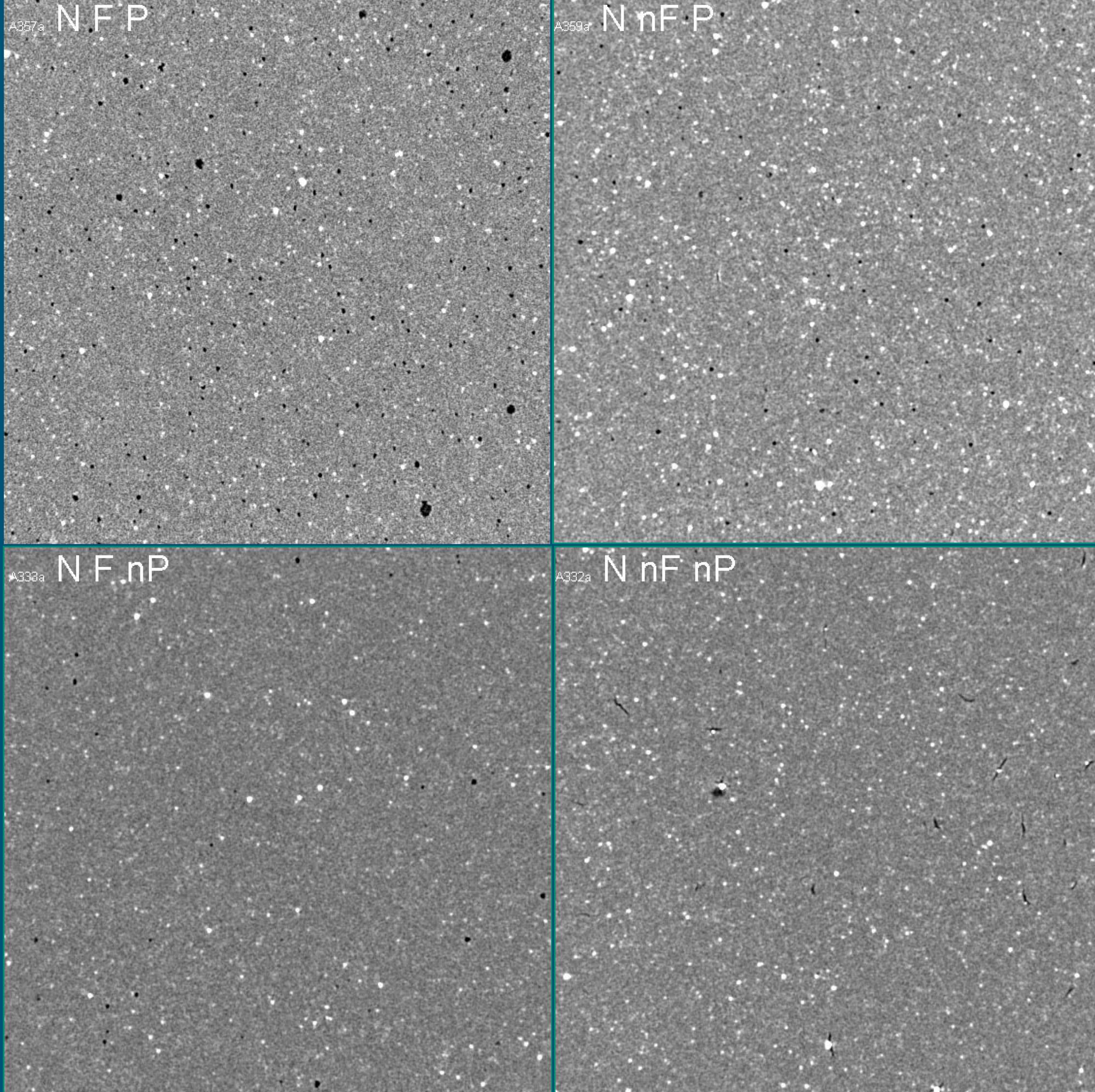
FP : many voids; some large voids are not isotropic.

nF P : many small voids.

F nP: fewer voids; medium sized.

nF nP : cracks; not so many isotropic voids.

Void/micro-crack distribution and sizes changes with formulation



Comparing static exposure to cycling exposure

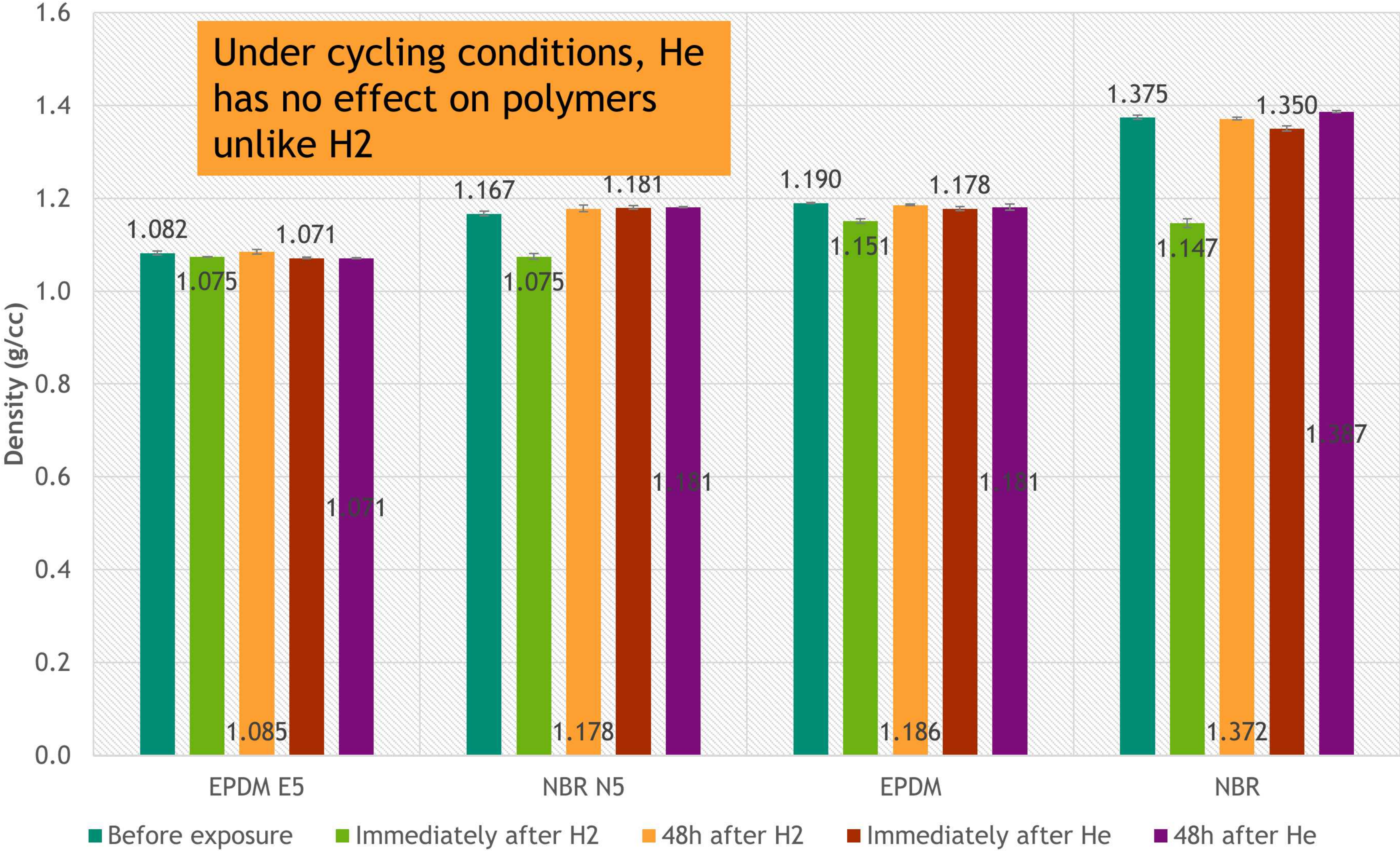
NBR and EPDM (Commercial and custom) specimens were exposed to :

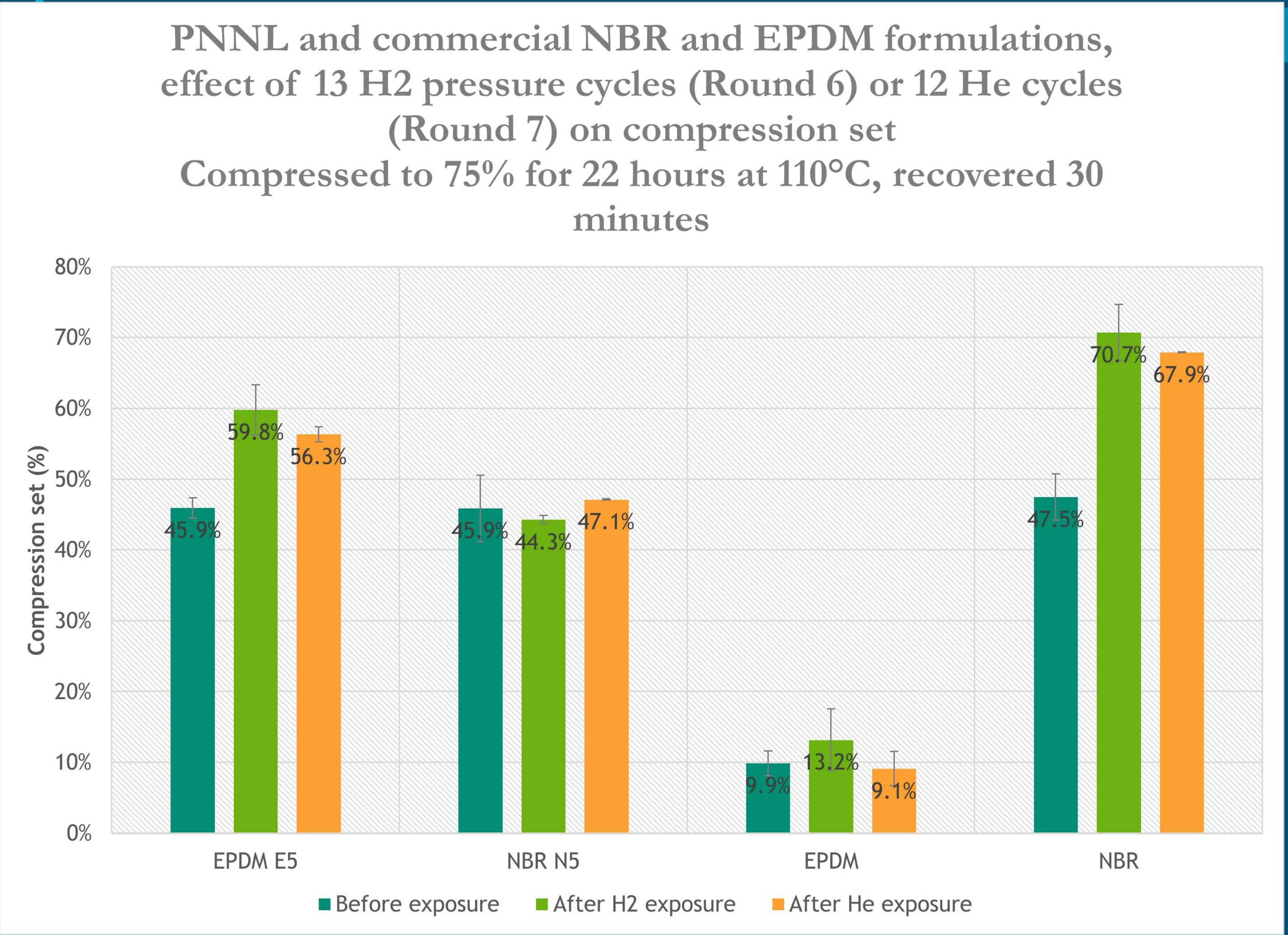
a. Static conditions with high pressure H2 at 103 MPa for one week at 20°C;

b. Cycling between 17 MPa and 86 MPa of H2 at 20°C for 13 cycles

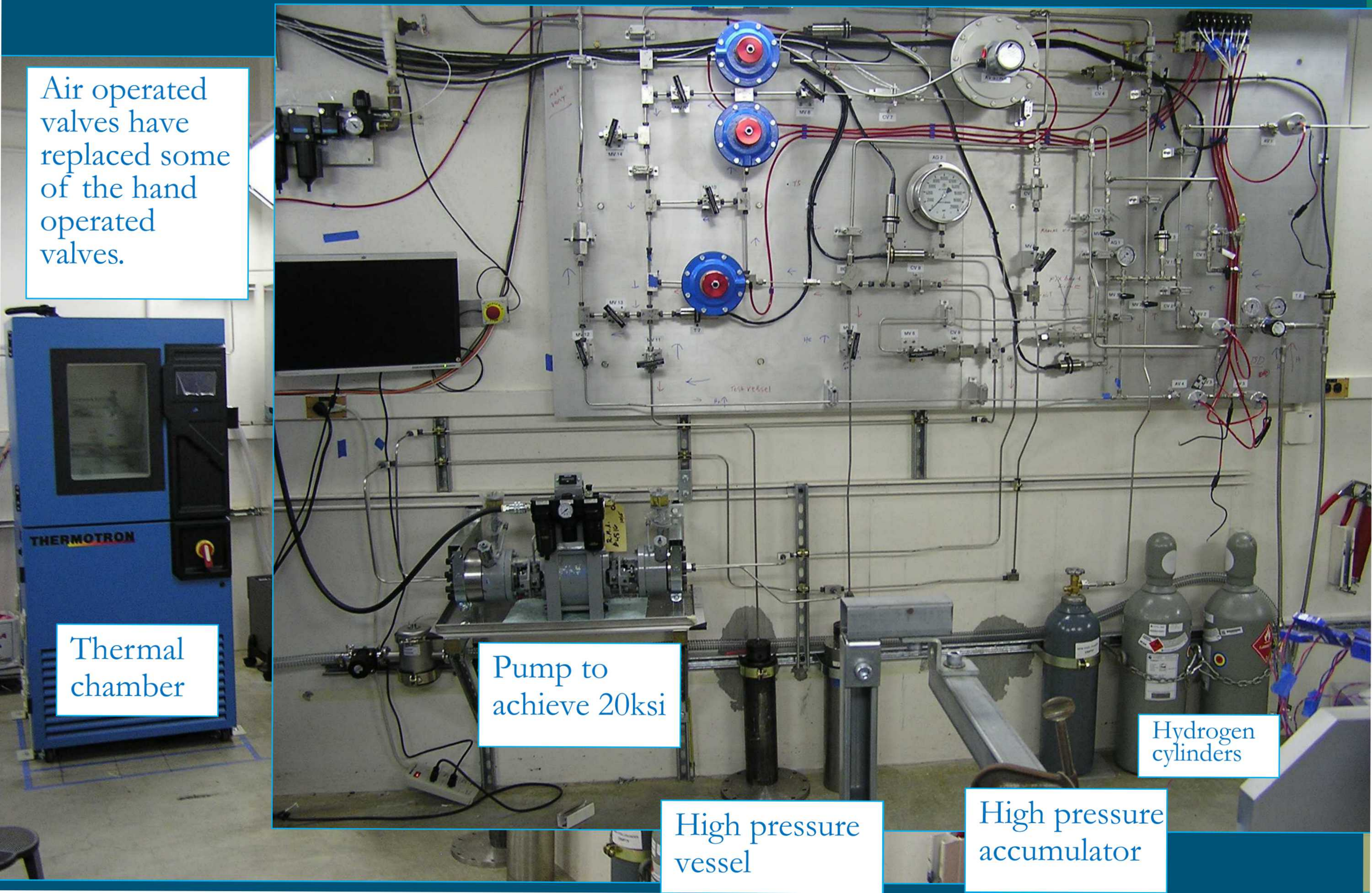
c. Cycling between the same pressures at 20C for 12 cycles in He

PNNL and commercial NBR and EPDM formulations, change in density after 13 H2 pressure cycles (Round 6) or 12 He cycles (Round 7)




PNNL and commercial NBR and EPDM formulations, effect of 13 H2 pressure cycles (Round 6) or 12 He cycles (Round 7) on compression set
Compressed to 75% for 22 hours at 110°C, recovered 30 minutes
80%
70%
60%
50%
40%
30%
20%
10%
0%
Compression set (%)
45.9%
59.8%
56.3%
45.9%
44.3%
47.1%
9.9%
13.2%
9.1%
47.5%
70.7%
67.9%
EPDM E5
NBR N5
EPDM
NBR
Before exposure
After H2 exposure
After He exposure

The new pressure cycling manifold along with the thermal chamber (to the left) for automatic cycling



Current **ongoing** work under the H-MAT program

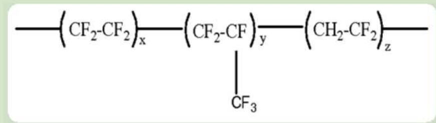
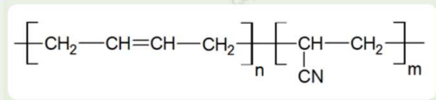
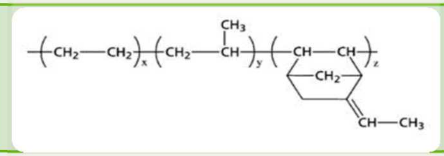
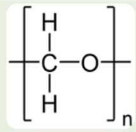
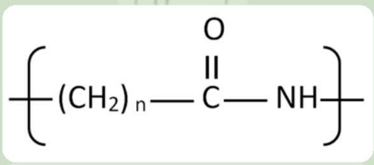
FY19 Other data on H2 cycling collected so far

- Nanoindentation effects on hardnes
- Micro CT: Avizo software allowing for determination of percent voids, percent particles, percent voided particles
- Outgassing and head space analysis of H2 exposed polymers
- Cycling in He (13 cycles) of NBR 5 and EPDM 5 to compare with H2 (13 cycles) completed, data collection in progress

THANK YOU FOR YOUR ATTENTION !!

BACK-UP SLIDES

Common polymers selected for evaluation

Polymer (chemical family)	Component in Hydrogen Infrastructure	Polymer Chemical Structure	Properties
Viton A (Elastomer)	O-rings, gaskets, seals		Fluoroelastomer with 66% fluorine, 75 Shore A hardness high chemical resistance wide service temperature (-29°C to 204˚C) low compression set
Buna-N Nitrile Butadiene Rubber (Elastomer)	O-rings, gaskets, seals		High acrylonitrile-content grade rubber superior chemical resistance medium-low flexibility
EPDM Ethylene Propylene Diene Monomer (Elastomer)	O rings		Ethylene content (45-85%) ensures processability Compatible with polar liquids Extremely resistant to heat, ozone, steam and weather
HDPE High Density Poly Ethylene (Thermoplastic)	Pressure tank liners	$-(CH_2-CH_2)_n-$	Possibly a filled PE80/PE100 grade High impact strength Excellent chemical resistance low moisture absorption properties
PTFE Polytetrafluoroethylene (Thermoplastic)	O-rings, seals	$-(CF_2-CF_2)_n-$	Premium virgin Type 1, grade I, unfilled High temperature resistance Chemically inert Low coefficient of friction
POM Polyoxymethylene (Thermoplastic)	Hoses		High strength, hardness and rigidity to -40C High crystallinity
Nylon 11 Polyamide (Thermoplastic)	Seals, gaskets, pressure tank liners, hose liners		Low moisture absorption Better UV resistance compared to other types of nylon Semi-crystalline nature