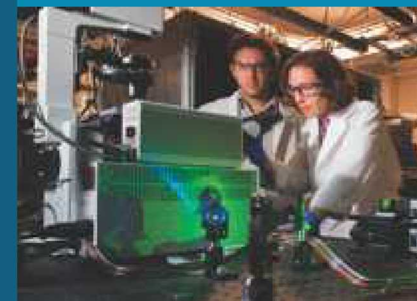
SAND2019-8603PE

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

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Sandia National Laboratories, CA

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

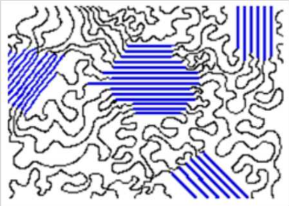
Strategy for Polymer compatibility with hydrogen

- Polymer microstructure
- Hydrostatic pressure effects
- Plasticization of polymers
- Permeation, diffusion and solubility effects
- Explosive decompression

•Polymers

•Material selection (Existing list)

•New materials for hydrogen service



Elucidation of hydrogen effects

H-MAT work (FY 2019)

Modeling and simulation

Compatibility of Polymers in Hydrogen environments

Test Environments

Low/high temperatures

Low/high pressures

De-pressurization rates

Rapid cycling (P, T, time)

Long-term aging in H_2

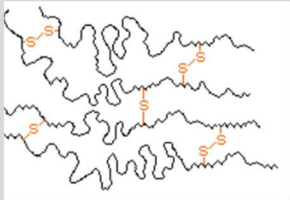
Gas mixtures

- Collaboration with SDOs (CSA, ASTM, ASME etc.)
- Existing test methods adapted for hydrogen
- Dissemination of test methods

Characterization

H2 Effects for Common Polymers (FY 16-18)

Thermal desorption spectroscopy



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

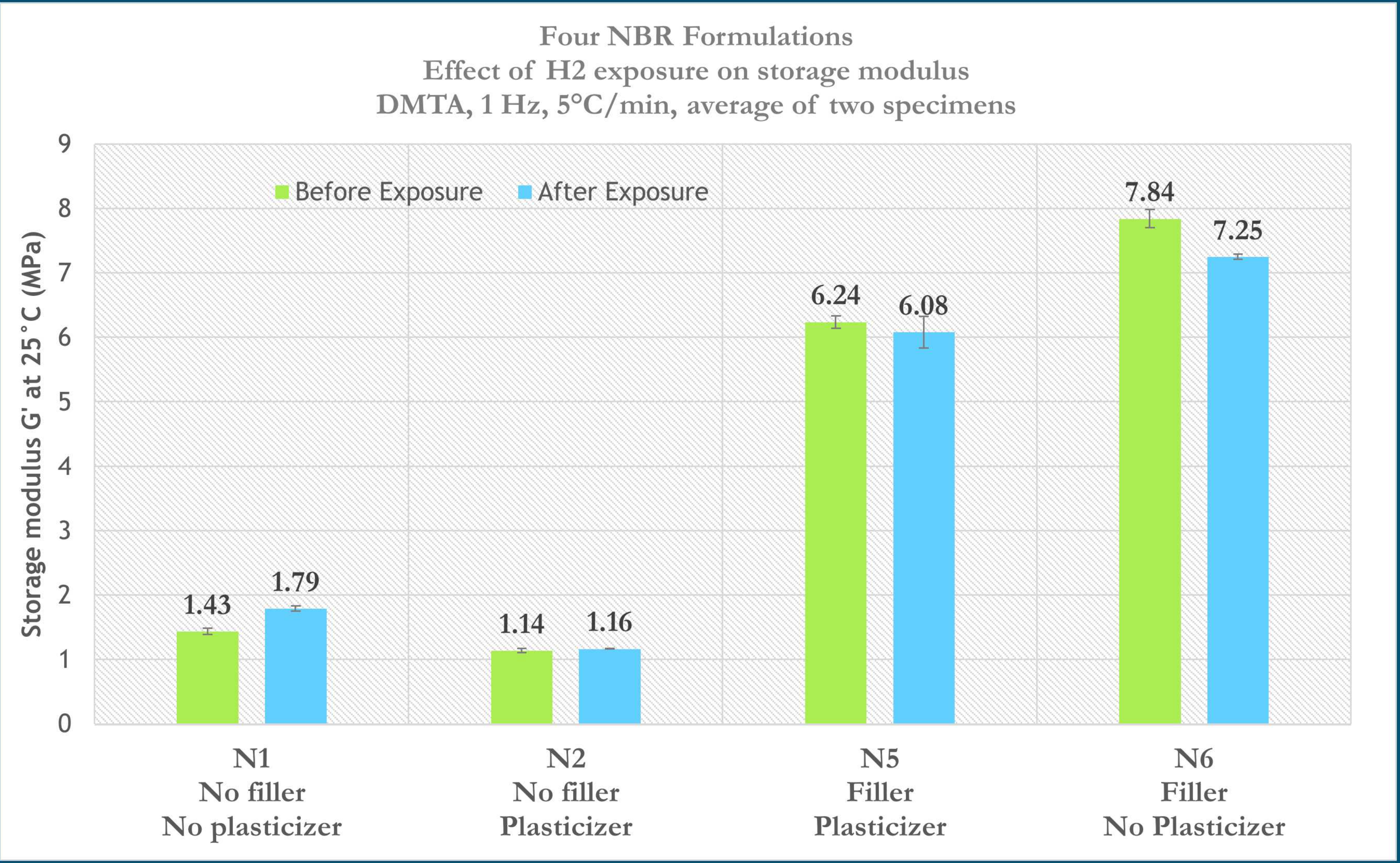
Linking H2 effects to polymer micro structure and length scales:

Conditions of exposure: one week-long cycle of static high pressure (100 MPa) @ ambient temperature

For e.g.

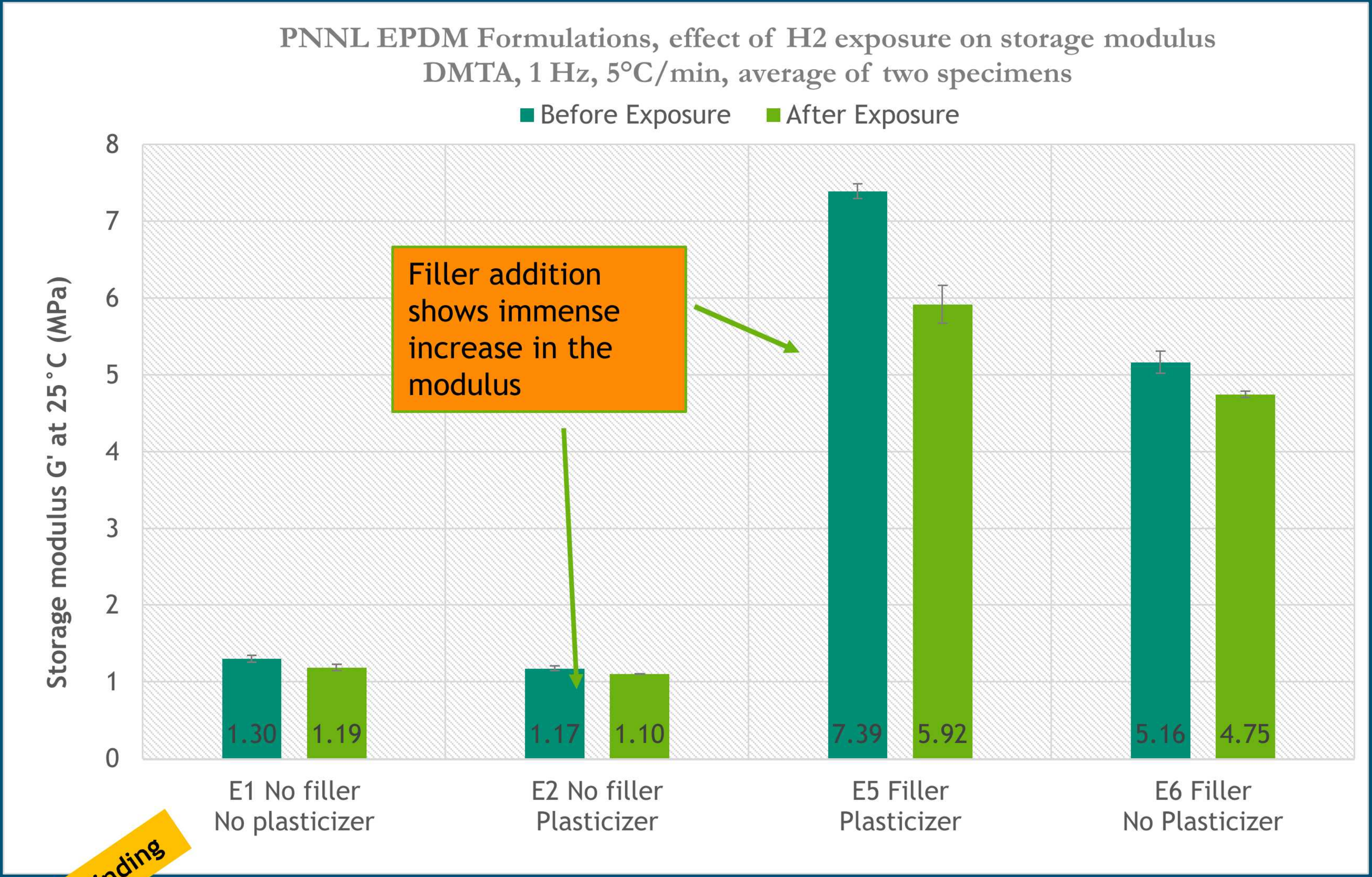
1. modulus – macro effect; bulk property
2. set – Lower length scales ??
3. density – macro effect ??
4. glass transition effect – lower length scales; macro effect of fillers and plasticizers ??

Hydrogen effects in Nitrile Rubber from fillers and additives: Storage modulus



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

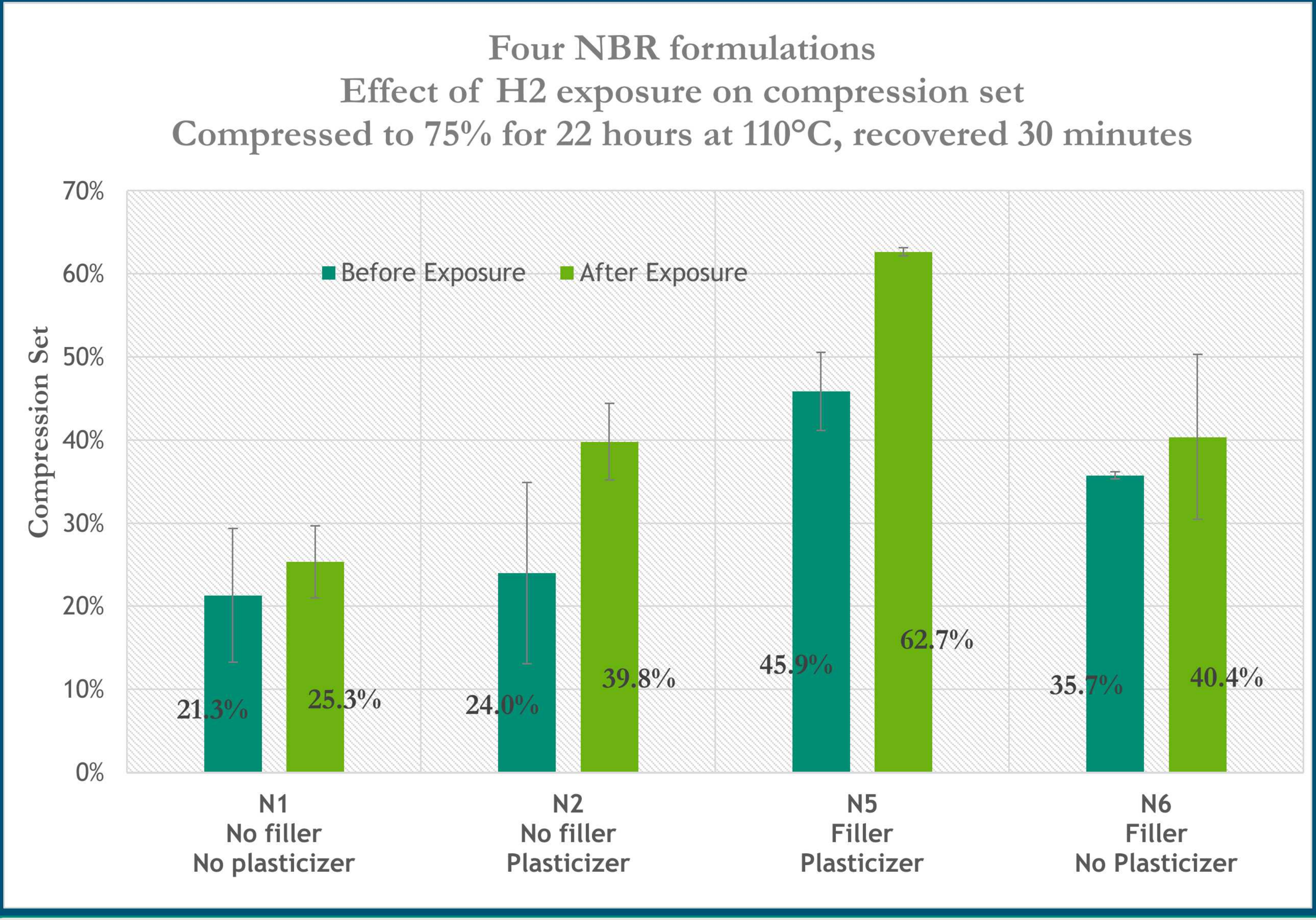
Hydrogen effects in EPDM from fillers and additives: Storage modulus



New finding

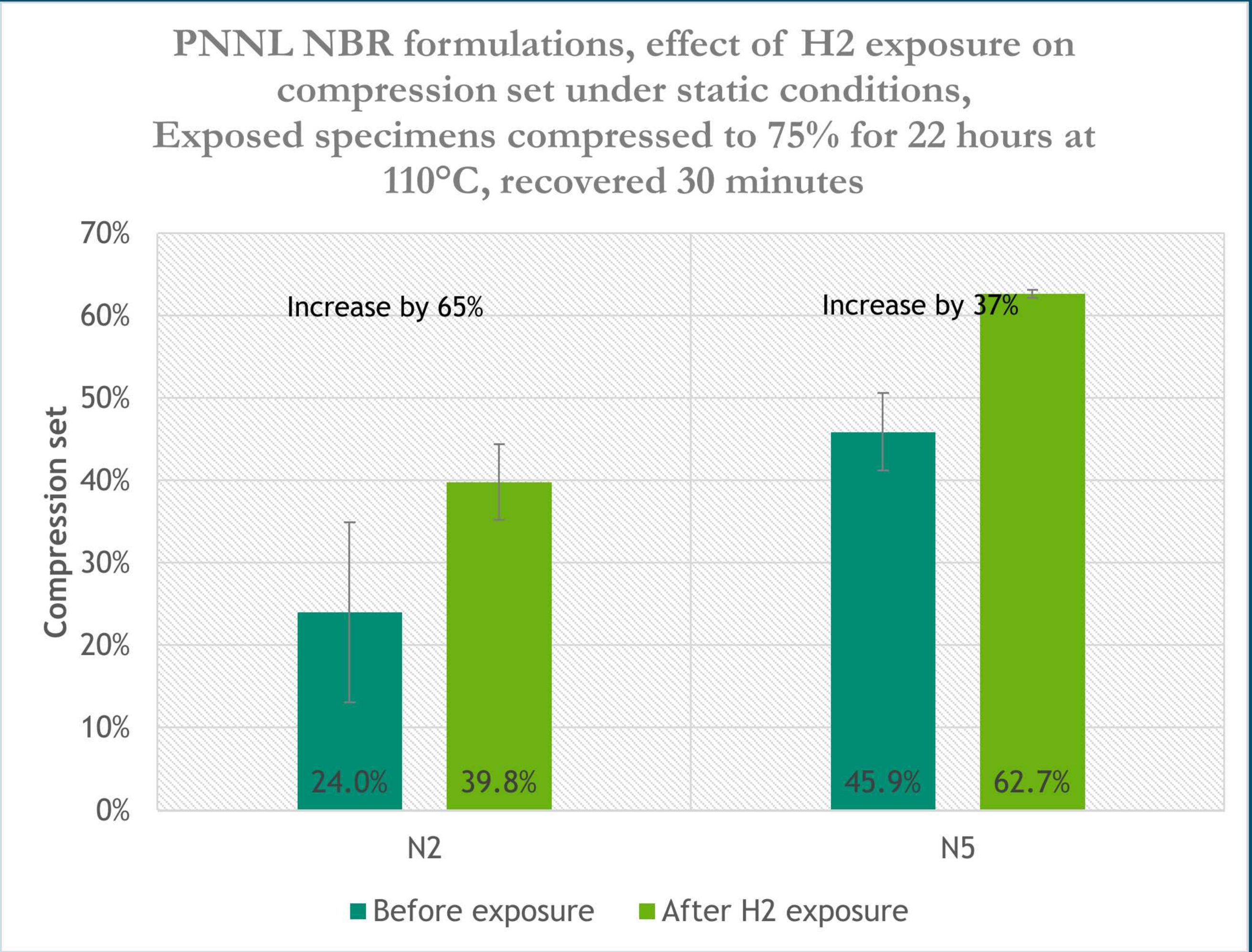
A 20% decrease in modulus is seen in filled plasticized EPDM after once cycle of H2 exposure – significant macro change, plasticization of EPDM with H2; permanent effect

Hydrogen effects in Nitrile Rubber from fillers and additives: Compression set



Compression set increased by ~37% due to H2 exposure for a filled plasticized NBR system: More of a free volume effect?? Significant and permanent effect on lower length scales ??

Effect of fillers and palsticizers in NBR : Static or non-cycling exposure

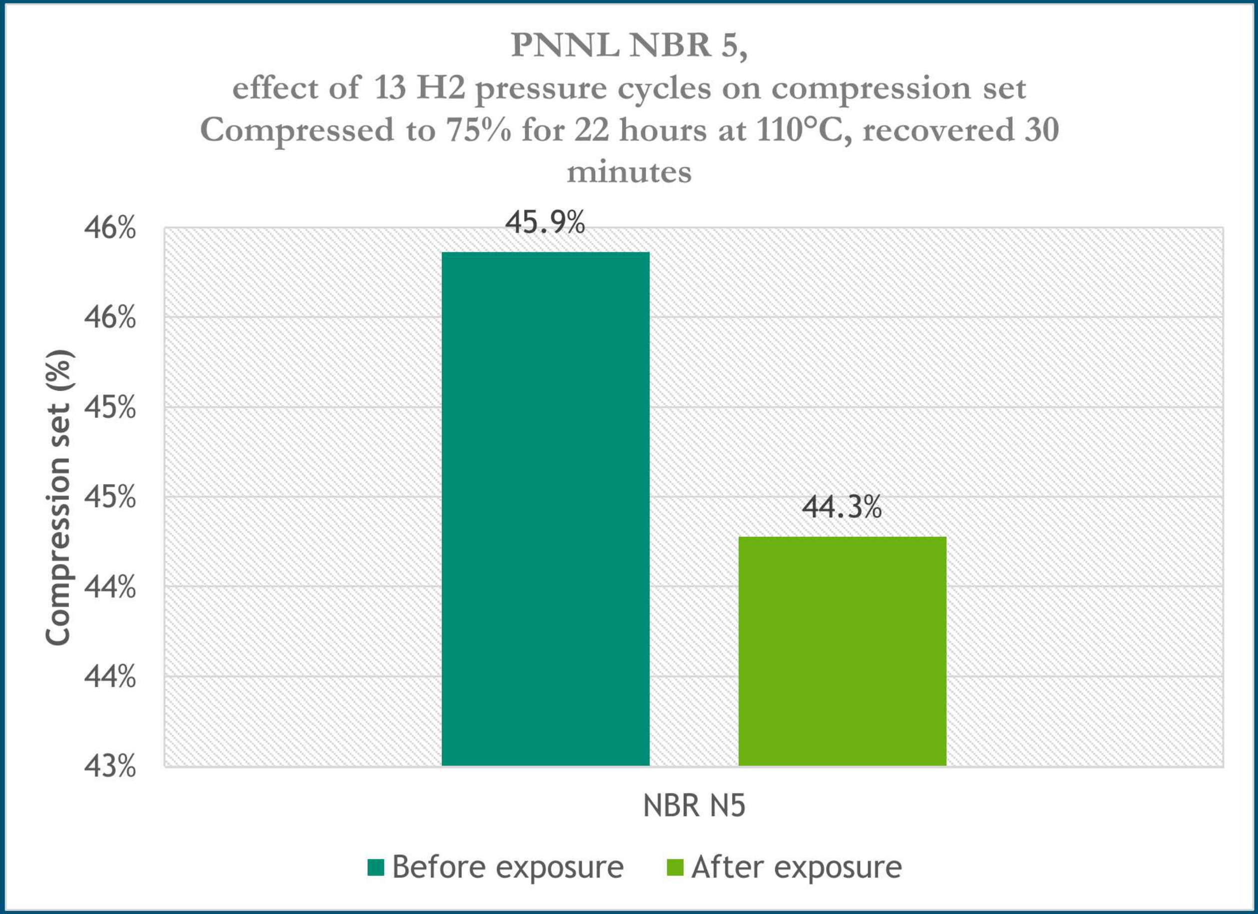


Plasticizers increase compression set and fillers mitigate compression set (decrease to 37%); seen as crack mitigation in micro CT

Slide 10

MNC1 Menon, Nalini Chulliyil, 7/22/2019

Effect of fillers and palsticizers in NBR : Cycling exposure

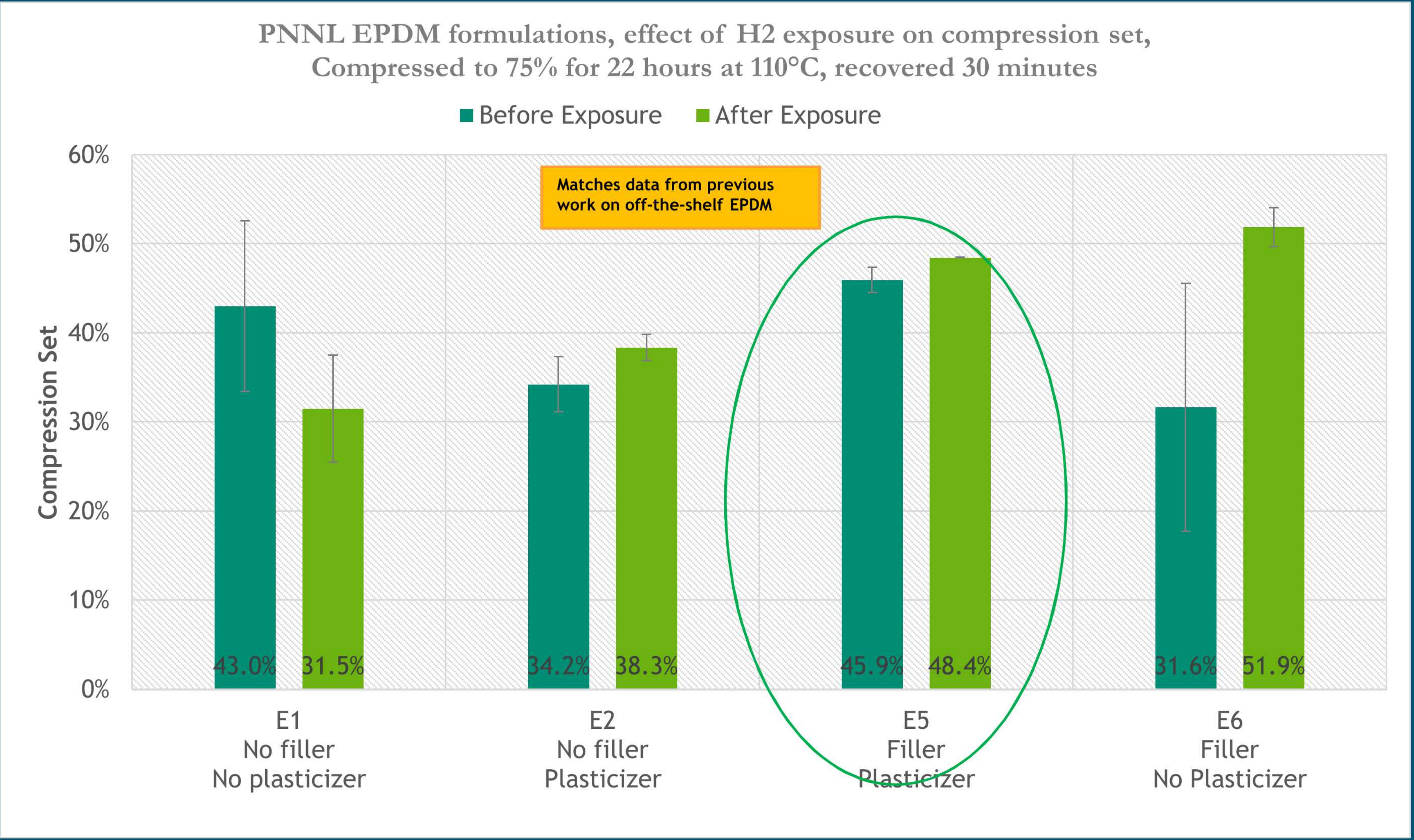


Overall, the compression set decreases slightly in filled and plasticized NBR in cycling tests – less number of cycles, length of each cycle and slow depressurization rate

Slide 11

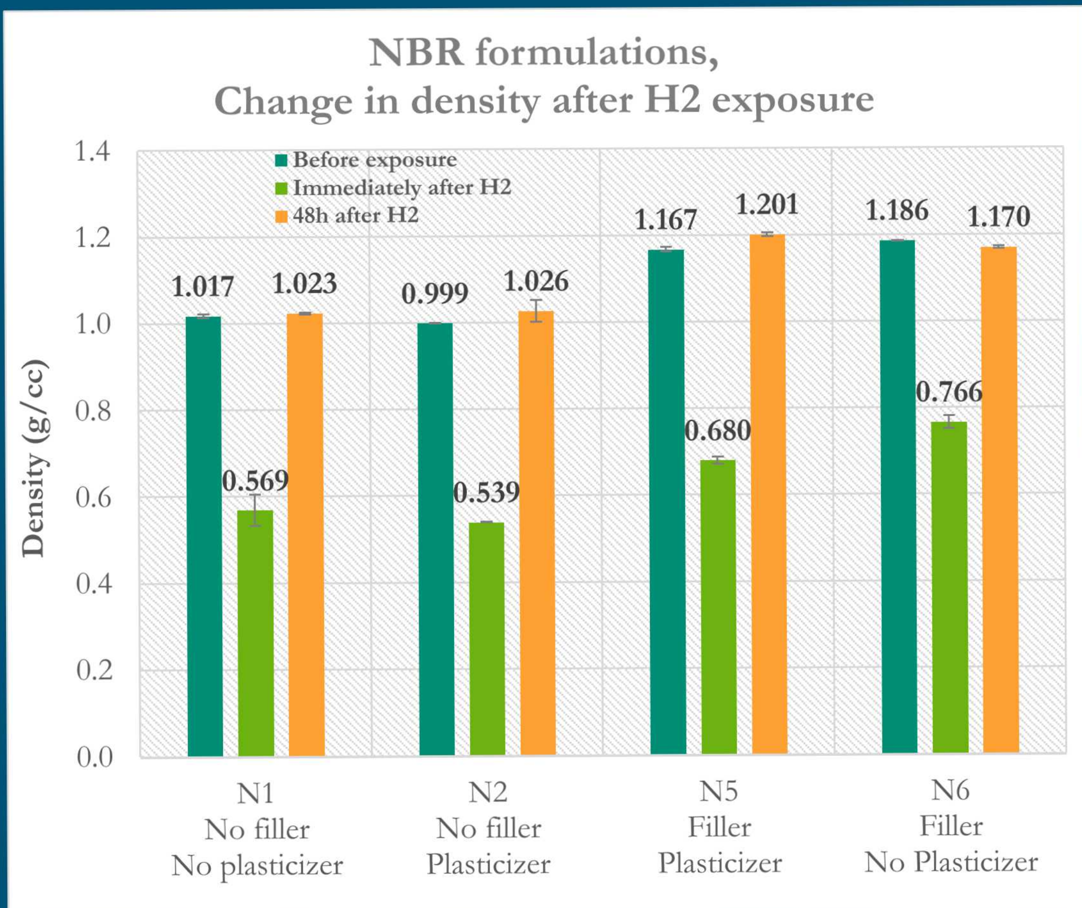
MNC1 Menon, Nalini Chulliyil, 7/22/2019

Hydrogen effects in EPDM from fillers and plasticizers: Compression set

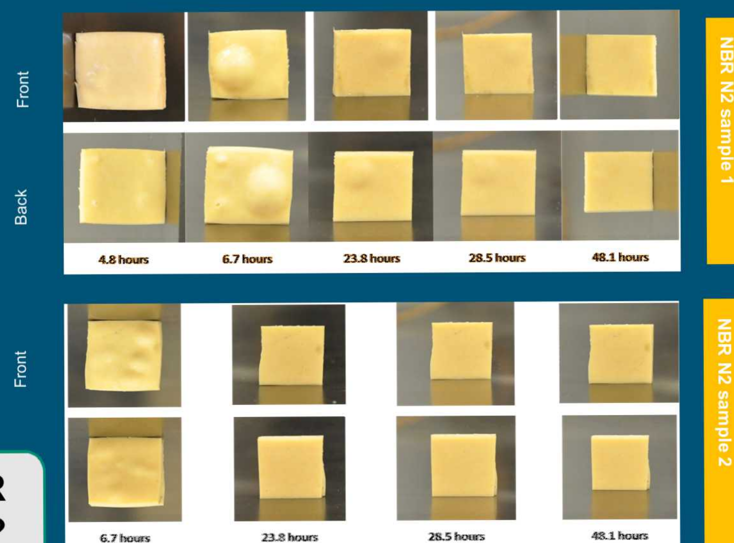


Compression set change due to H2 exposure for a filled, plasticized EPDM system is insignificant: lower free volume than NBR due to high crosslink density, less effect on lower length scales?

Hydrogen effects in Nitrile Rubber from fillers and additives: Density



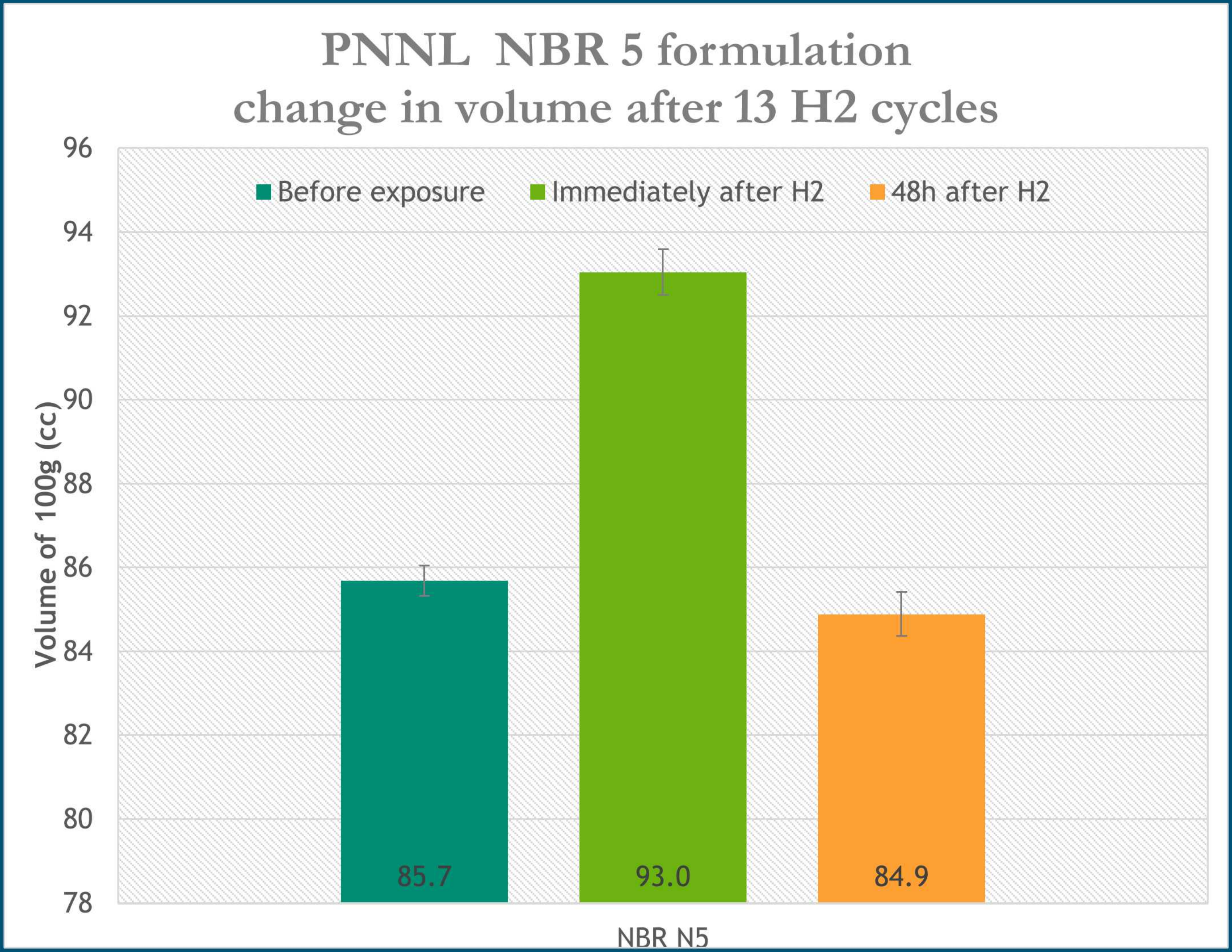
#	Filler	Plasticizer	Percent increase in volume	Recovery in volume
N1	No	No	79%	99%
N2	No	Yes	85%	97%
N5	Yes	Yes	72%	97%
N6	Yes	No	55%	101%



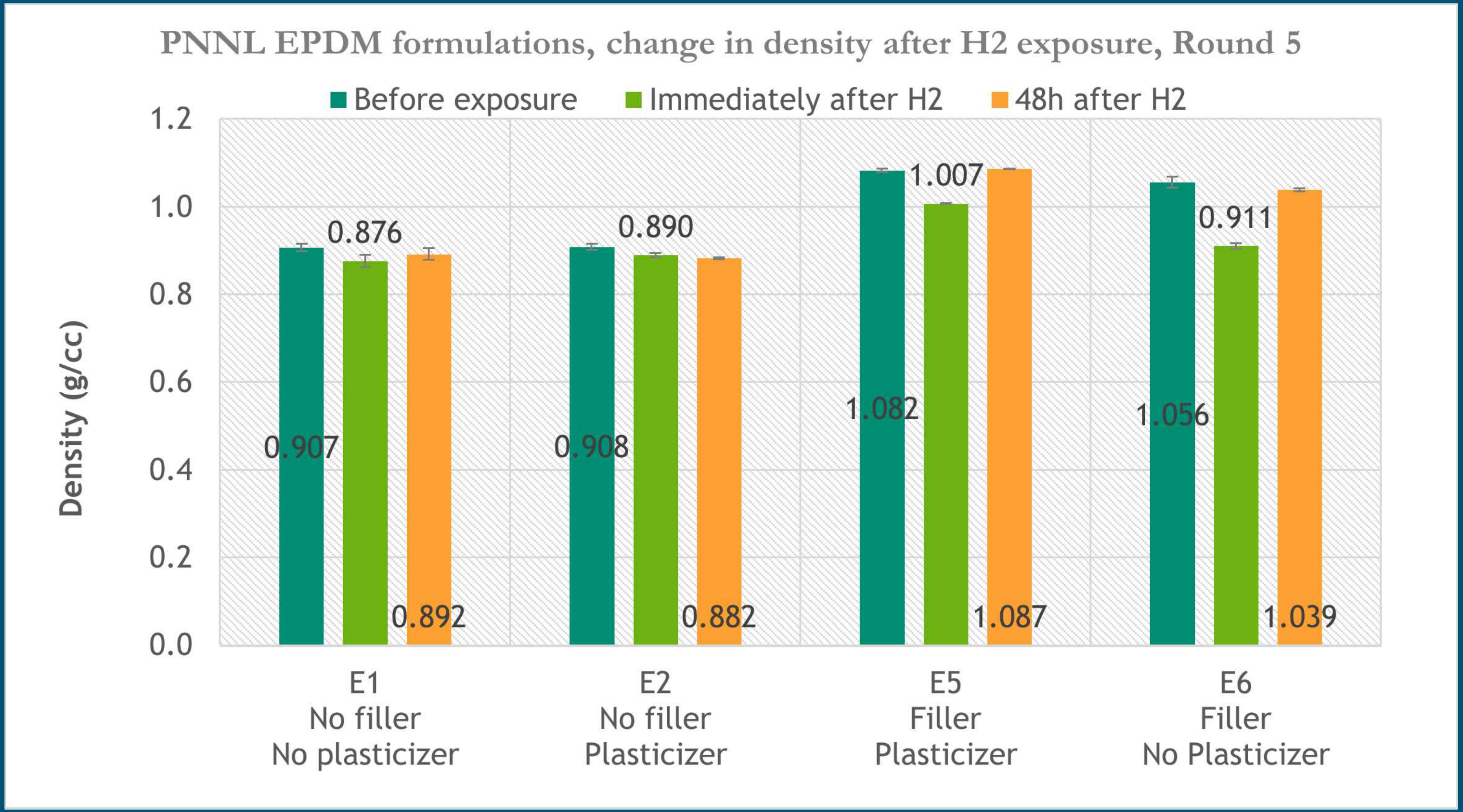
Picture showing the evolution of H2 from NBR N2 over 48 hours

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

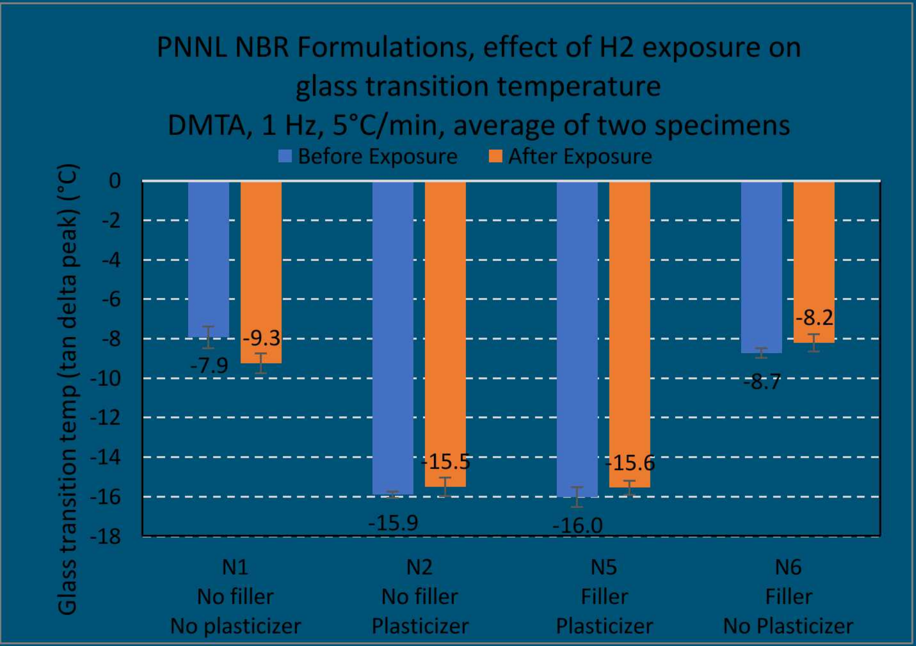


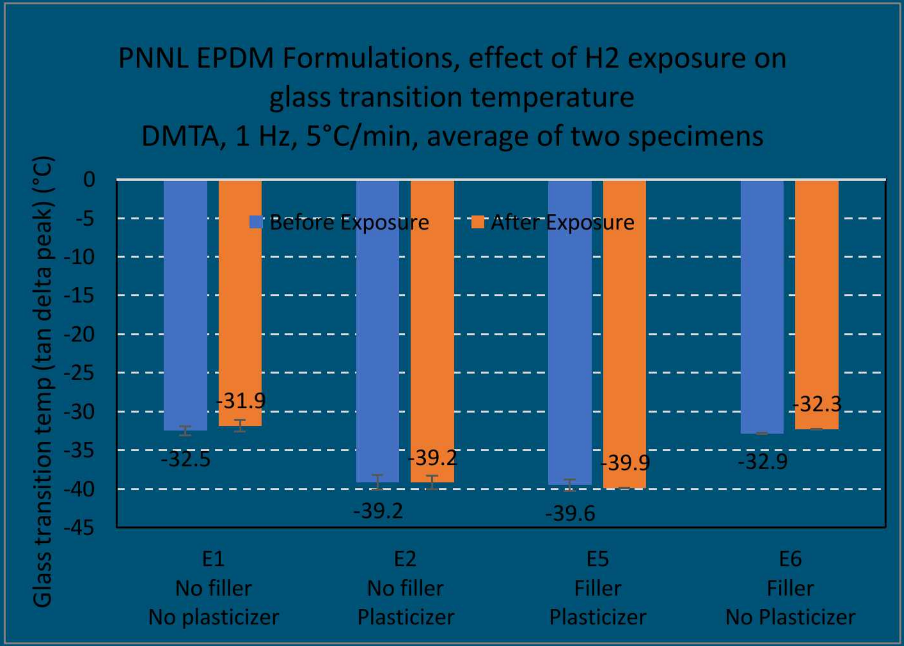
#	Filler	Plasticizer	Percent increase in volume	Recovery in volume
E1	No	No	4%	102%
E2	No	Yes	2%	103%
E5	Yes	Yes	8%	100%
E6	Yes	No	16%	102%

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

Glass transition temperature changes after H2 exposure

Matches data from previous work





- **For filled, plasticized EPDM and NBR systems, there is no significant change in T_g due to one cycle of H2 exposure**
- **Filler presence does not alter Tg; but, plasticizer decreases the T_g of EPDM and NBR significantly**

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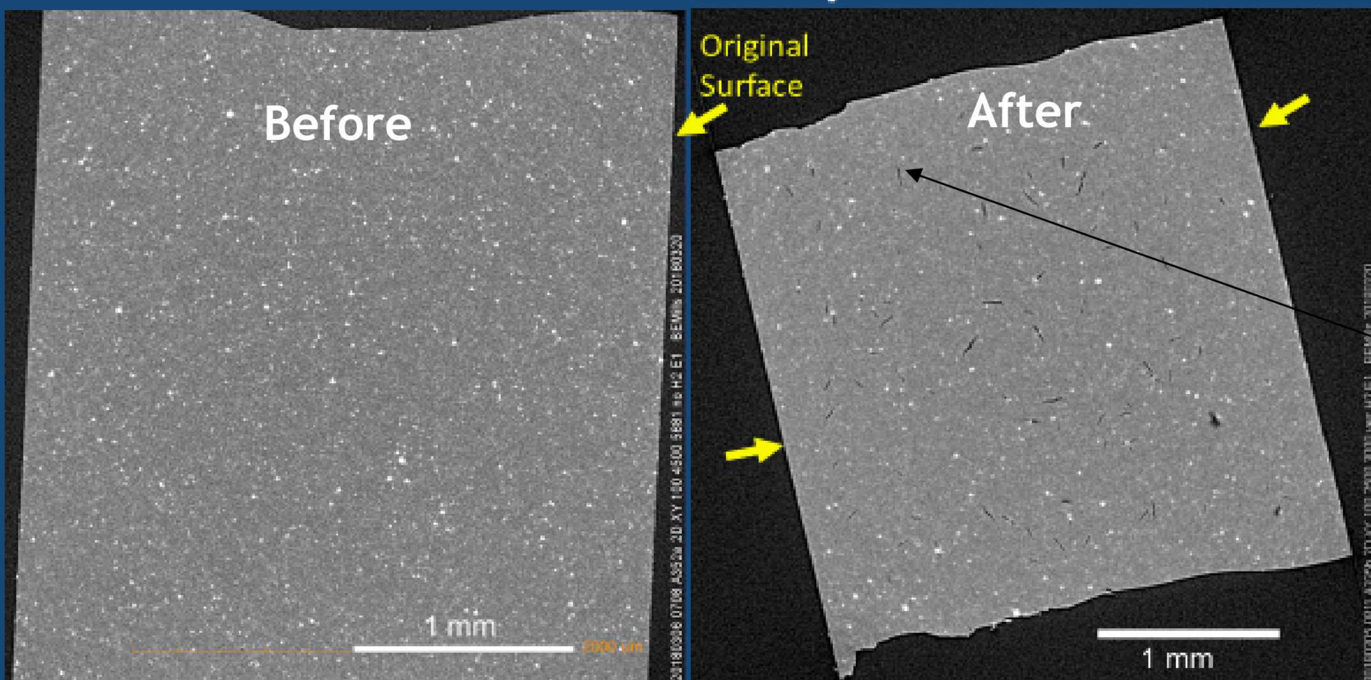
Micro-CT images for EPDM after H_2 exposure

H_2 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 H_2 exposure has significant microcrack damage

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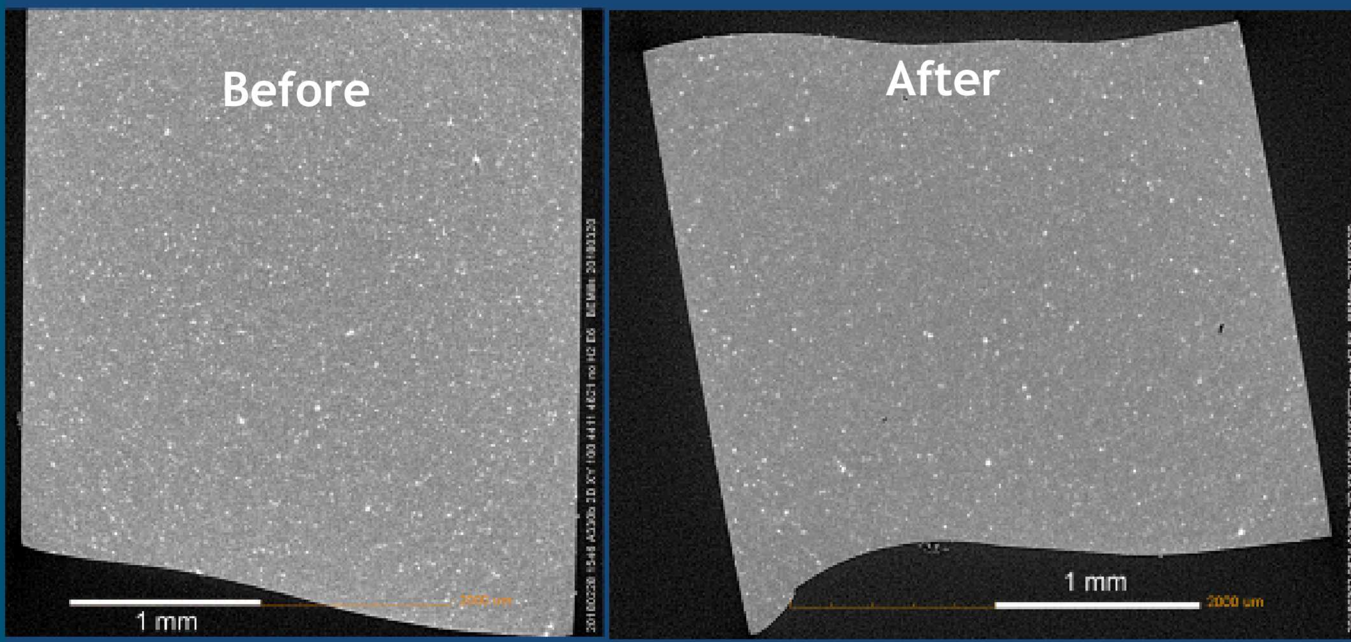
Micro-CT images for EPDM after H2 exposure

H2 exposure of EPDM E6 generates fewer but larger voids.



There is no preferred position within the sample.

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

- 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)

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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.

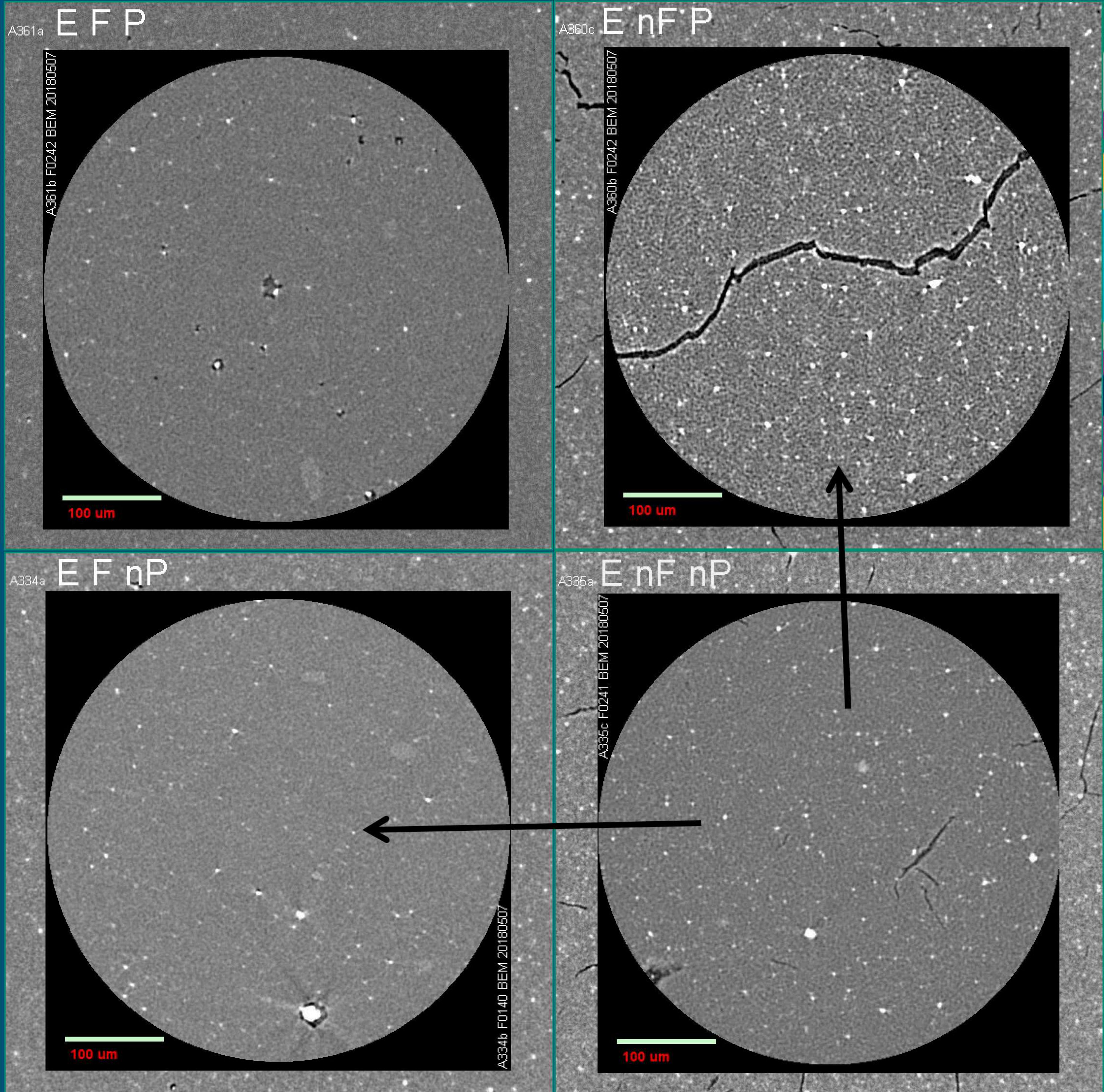
nF P worst case with long cracks.

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.

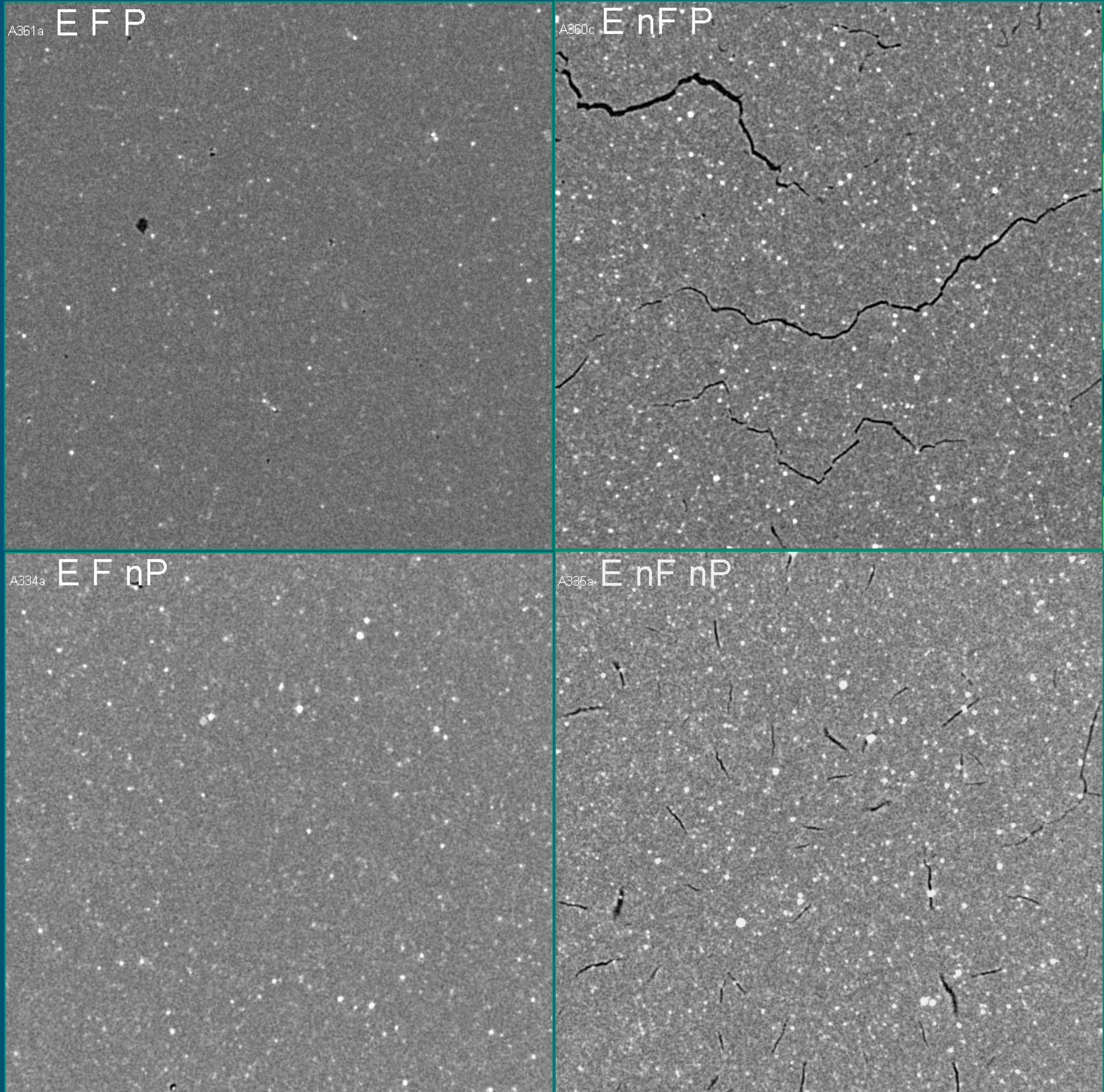
nF P worst case with long cracks.

F nP very few voids, small.

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

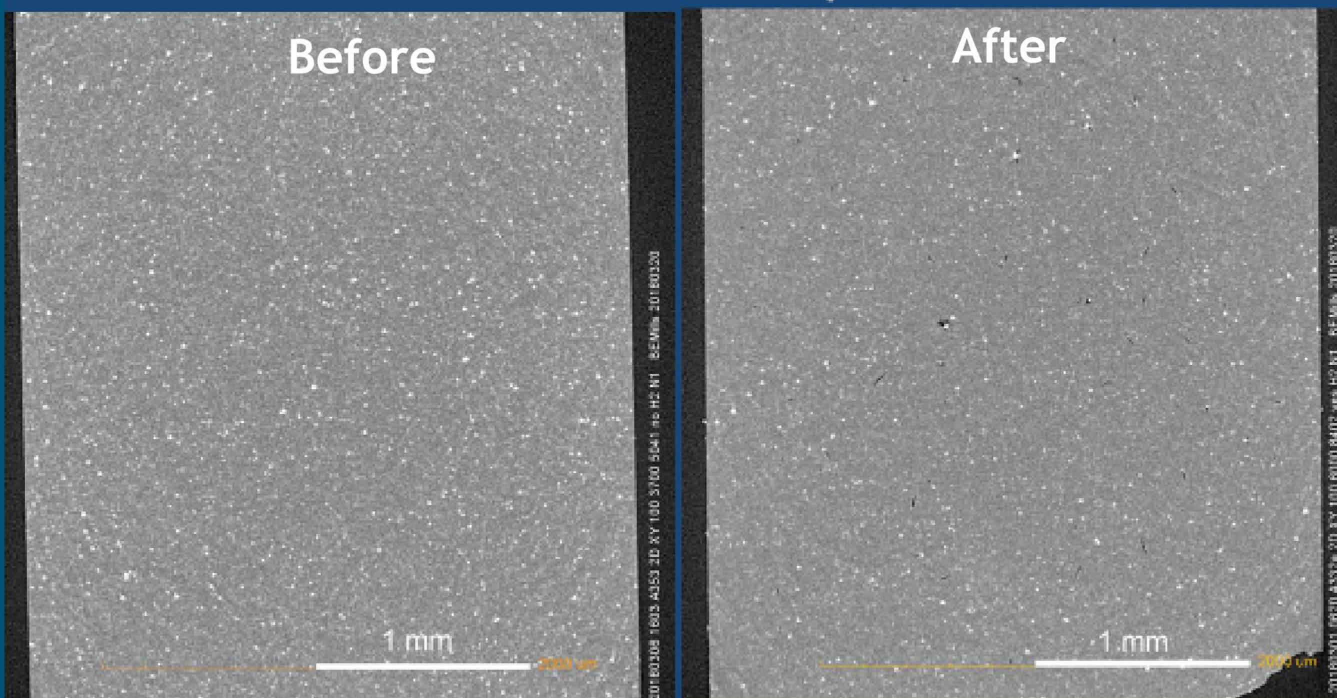
FP 2	P 4
F 1	3

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

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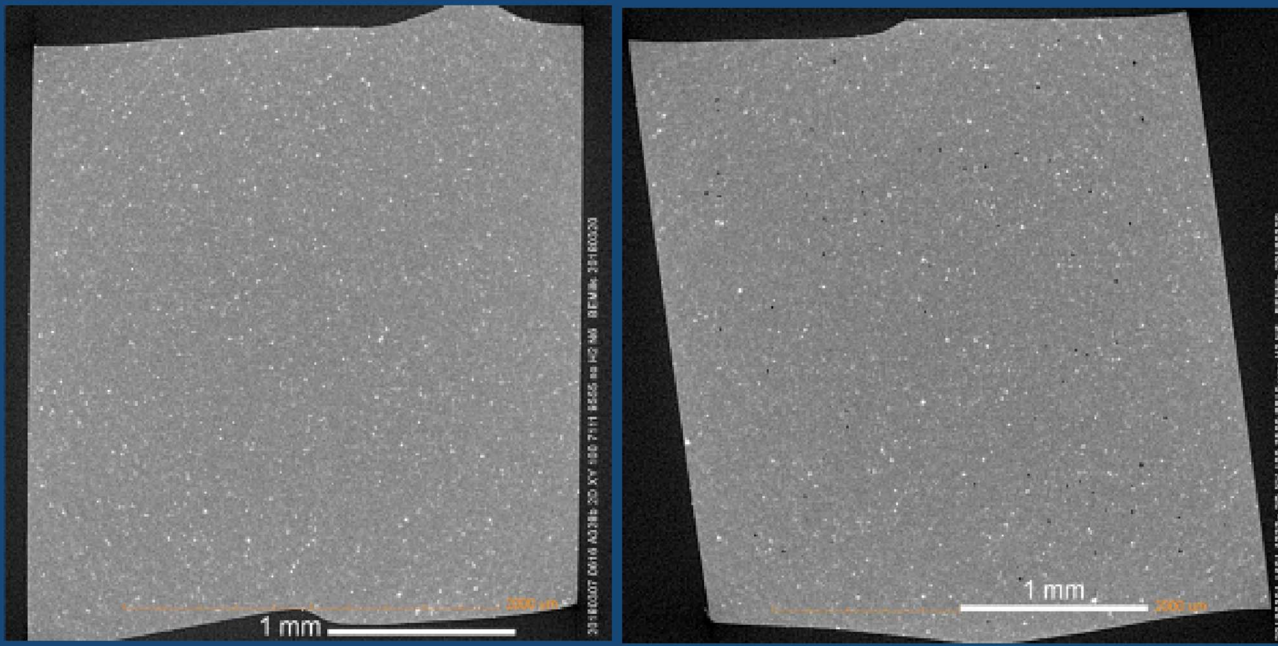
Accomplishments and Progress
Micro-CT images for NBR after H2 exposure

H2 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 H2 exposure

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NBRs compared

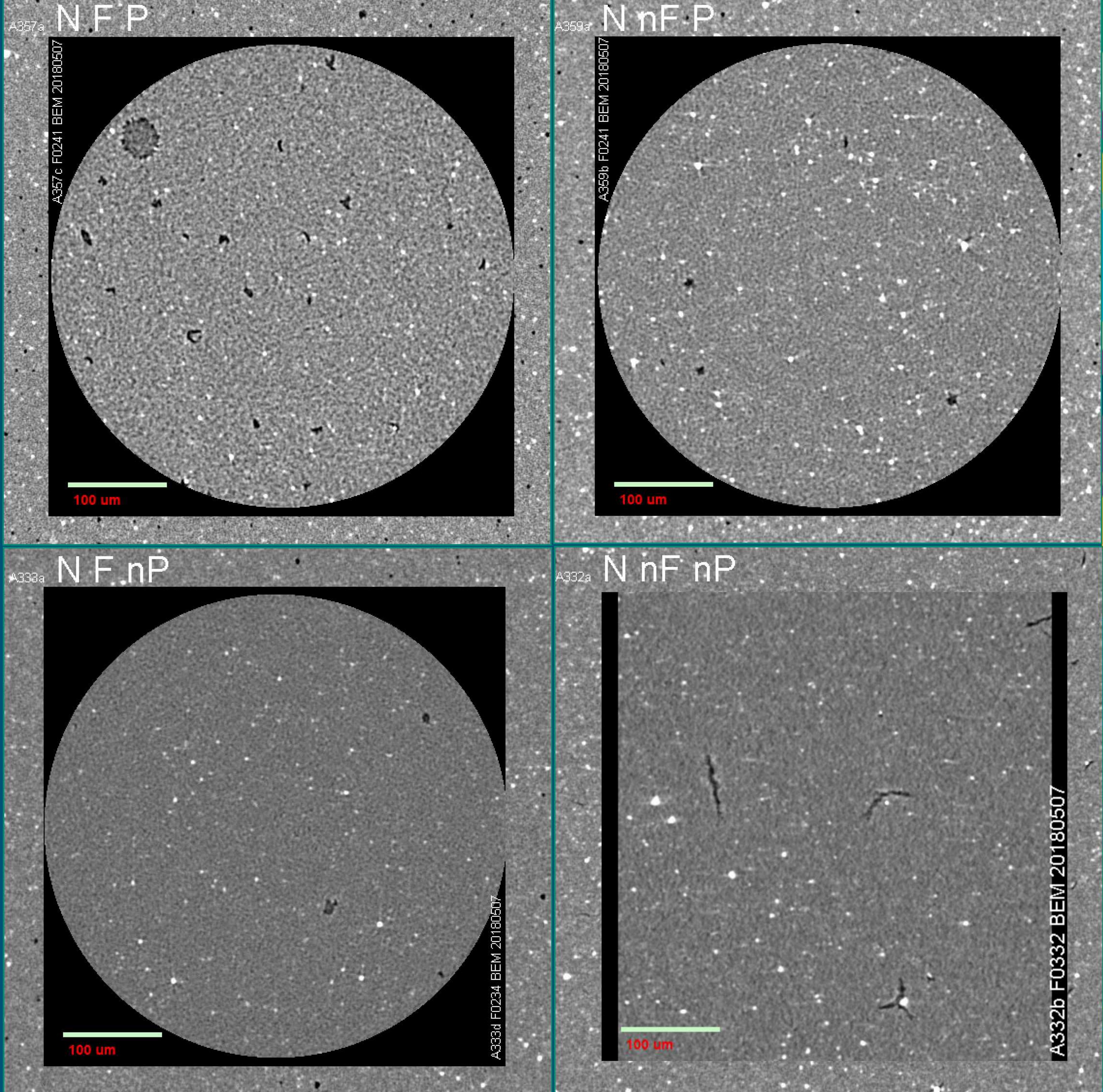
FP: many voids; some large voids have serrated edges. Closest to commercial formulation.

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

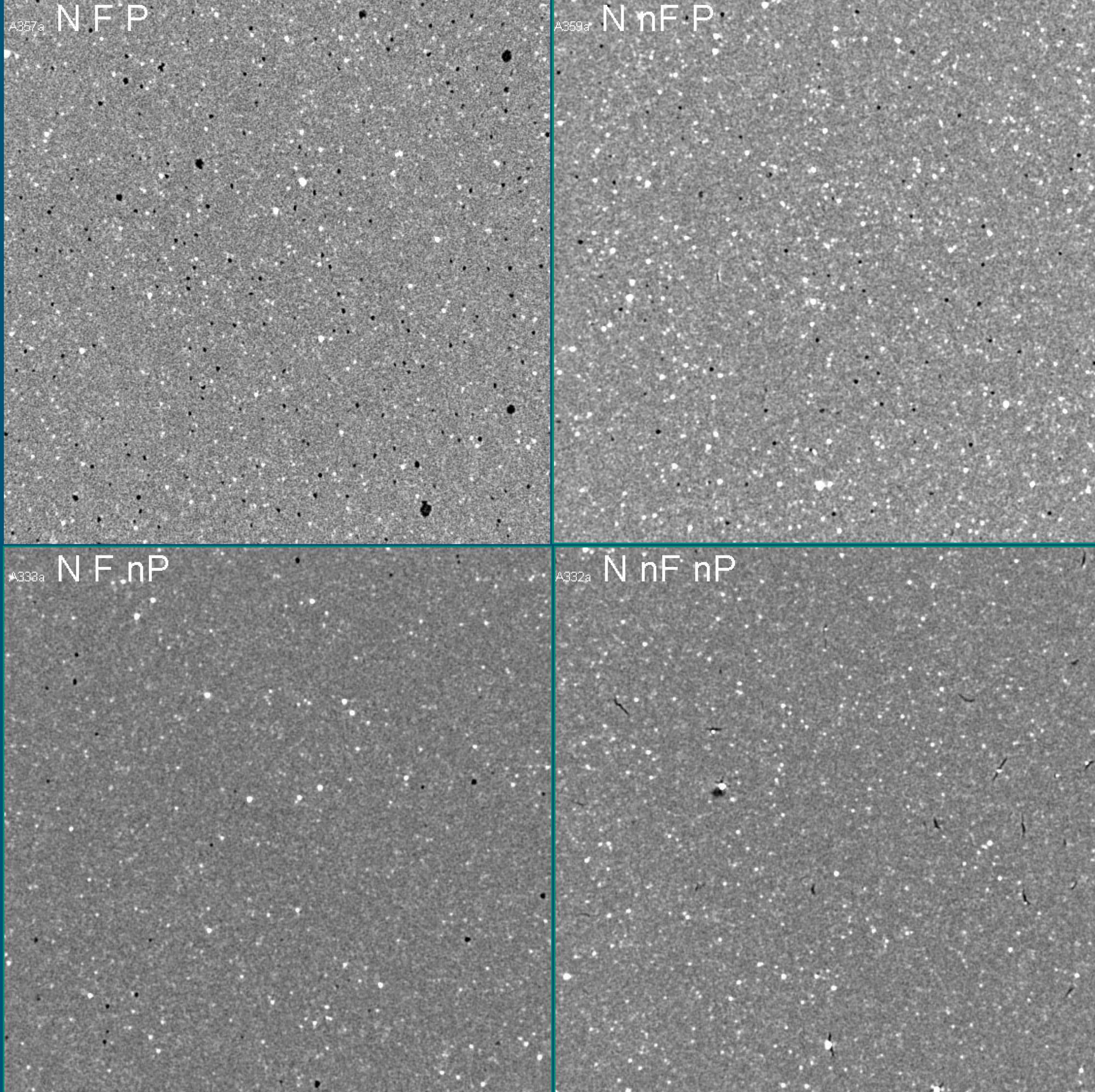
FP : many voids; some large voids are not isotropic.

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



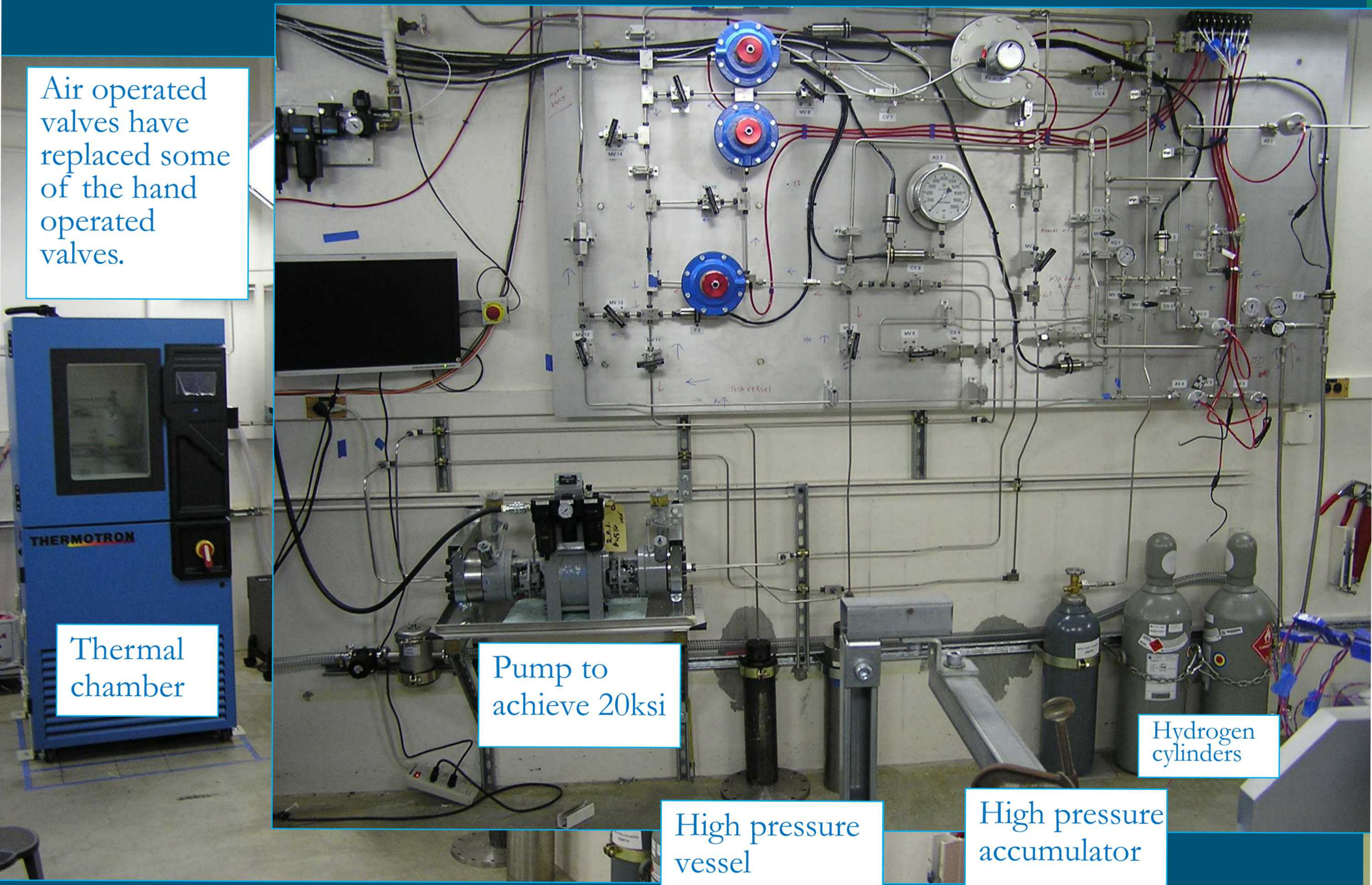
Comparing static exposure to cycling exposure

NBR specimens were exposed to :

a. Static conditions with high pressure H_2 at 103 MPa for one week at 20°C;

b. Cycling between 17 MPa and 86 MPa at 20°C for 12 cycles

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



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

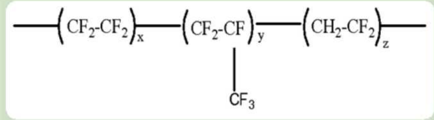
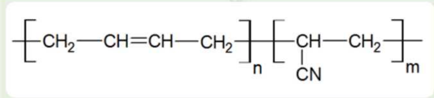
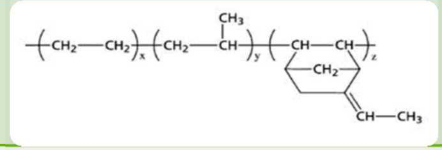
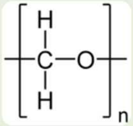
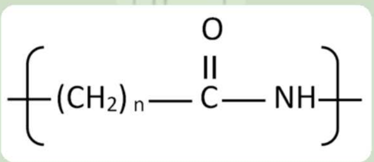
FY19 Other data on H2 cycling collected so far

- Nanoindentation effects on hardness
- Micro CT: Avizo software allowing for determination of percent voids, percent particles, percent voided particles etc
- 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	$-(CH_2\text{-}CH_2)_n-$	Possibly a filled PE80/PE100 grade High impact strength Excellent chemical resistance low moisture absorption properties
PTFE Polytetrafluoroethylene (Thermoplastic)	O-rings, seals	$-(CF_2\text{-}CF_2)_n-$	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