SAND2020-4569C

Hydrogen Materials Consortium

Performance of select thermoplastics and elastomers in high-pressure hydrogen cycling environments

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HMat

Hydrogen Materials Consortium

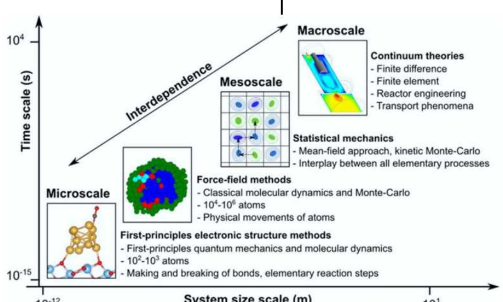
Compatibility of Polymers in Hydrogen

Lead : Pacific Northwest NATIONAL LABORATORY

Partners : Sandia National Laboratories, Oak Ridge National Laboratory

MODELING

- Atomistic scale
- Micro scale
- Phase Field Modeling
- Continuum scale



Task P1

Mechanisms of hydrogen-induced degradation of polymers

Task P2

Computational multiscale modeling

Task P3

Hydrogen-resistant polymeric formulations

CRITICAL GAPS

- Degradation failure modes
- Explosive decompression
- Transport properties
- Friction and wear
- Fracture and fatigue

MANY VARIABLES

- Polymer sources
- Polymer types
- Composition (additives)
- Compounding methods
- Environments (cycling)

Accomplishment

Executive Summary : Cycling H_2 exposures

- Custom EPDM formulations and exemplar thermoplastics were exposed to high pressure cycling H_2 followed by ex-situ characterization of polymer physical and chemical properties

- For EPDM samples, the highly cross-linked tight polymer network with limited free volume plays a significant role in providing H_2 resistance
    - Minimal swell or specific volume change seen with H_2
    - Nominal change in T_g after H_2 indicates polymer network has not changed
    - Significant decrease in storage modulus indicates plasticization of matrix
    - Compression set increase after H_2 indicates plasticization of matrix
    - Filler-containing formulations show maximum change indicating interaction of carbon and silica with H_2

- The six thermoplastics tested (POM, PTFE, HDPE, PEEK, Nylon 6,6 and Nylon 11) do not show substantial changes; however,
    - Onset of chemical changes was identified for H_2 cycled polymers
    - Chemical changes were seen best with Fourier Transform Infra Red Spectroscopy (FTIR) and X-ray Diffraction (XRD)

Custom EPDM elastomers (Takaishi E1, E2, E5 and E6) Test Conditions, Ex-situ Characterization techniques

Conditions of exposure:

1. one week-long exposure to static high pressure (100 MPa) @ ambient temperature (Round 5)
2. 100 cycles, 86 MPa to 17 MPa and back, ambient temperature, rate of pressurization = 13.79 MPa/min; rate of depressurization = 2.29 MPa/min (Round 11)

Compression set

- ASTM D395
- Measure of permanent set of material
- Physical property change
- Can indicate changes in polymer amorphous matrix

Density

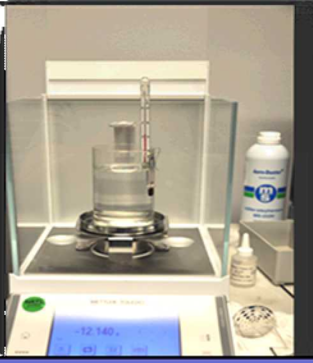
- ASTM B962-17 Immersion method
- Measure of change in density or specific volume of the polymer
- Can indicate changes in polymer matrix
- Impermanent change

Dynamic Mechanical Thermal Analysis

- Polymer viscoelastic behavior
- Glass transition temperature (T_g), complex modulus data
- Can indicate polymer micro structural changes

Sample holder with O ring specimens

Compression set test for elastomers



Density measurements set-up

Micro-CT, FTIR spectroscopy, nanoindentation, XRD analyses are in progress

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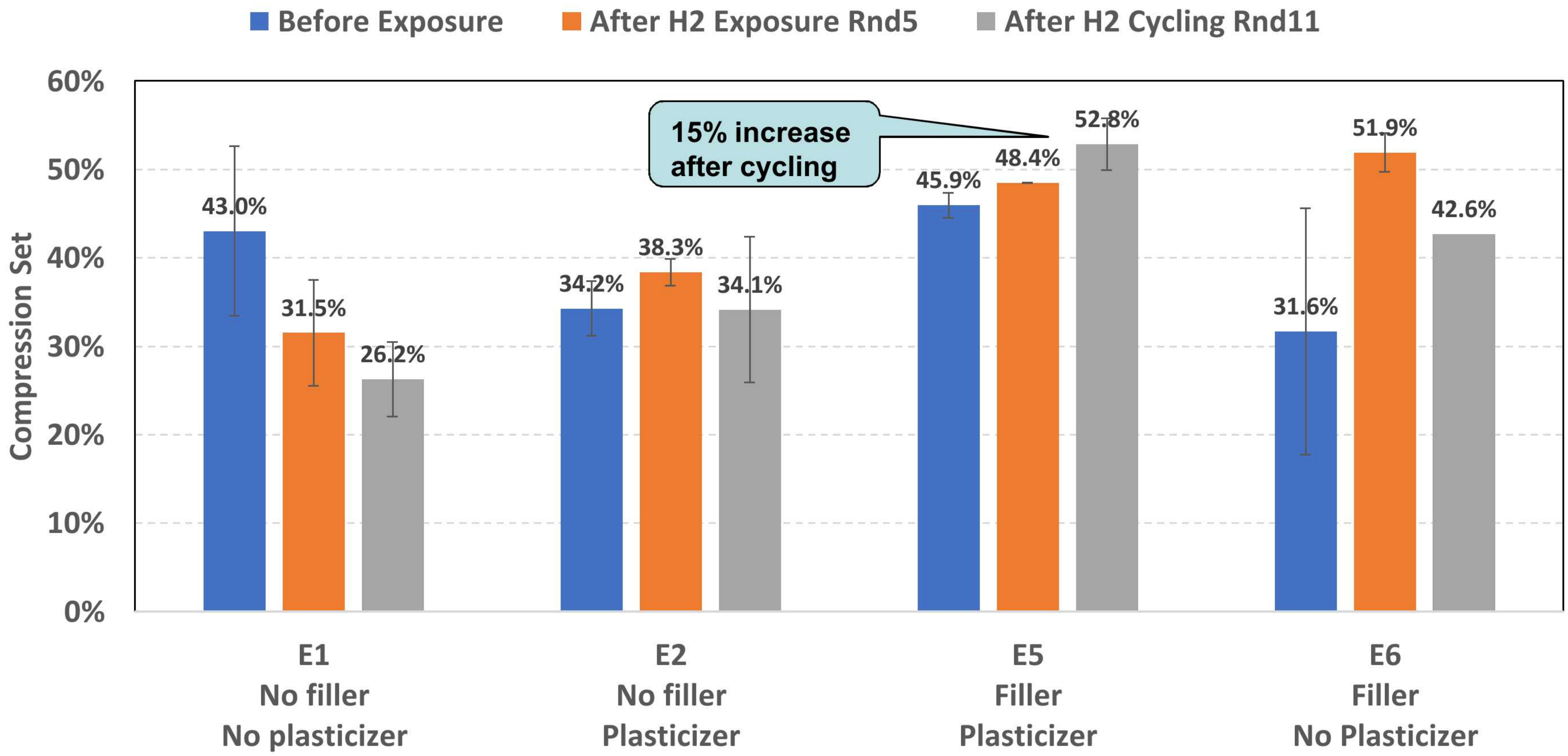
EPDM Compression set cycling vs. static H_2 exposure

PNNL EPDM formulations
effect of H2 exposure (Rnd5) and H2 cycling (Rnd11) on compression set
Compressed to 75% for 22 hours at 110°C, recovered 30 minutes

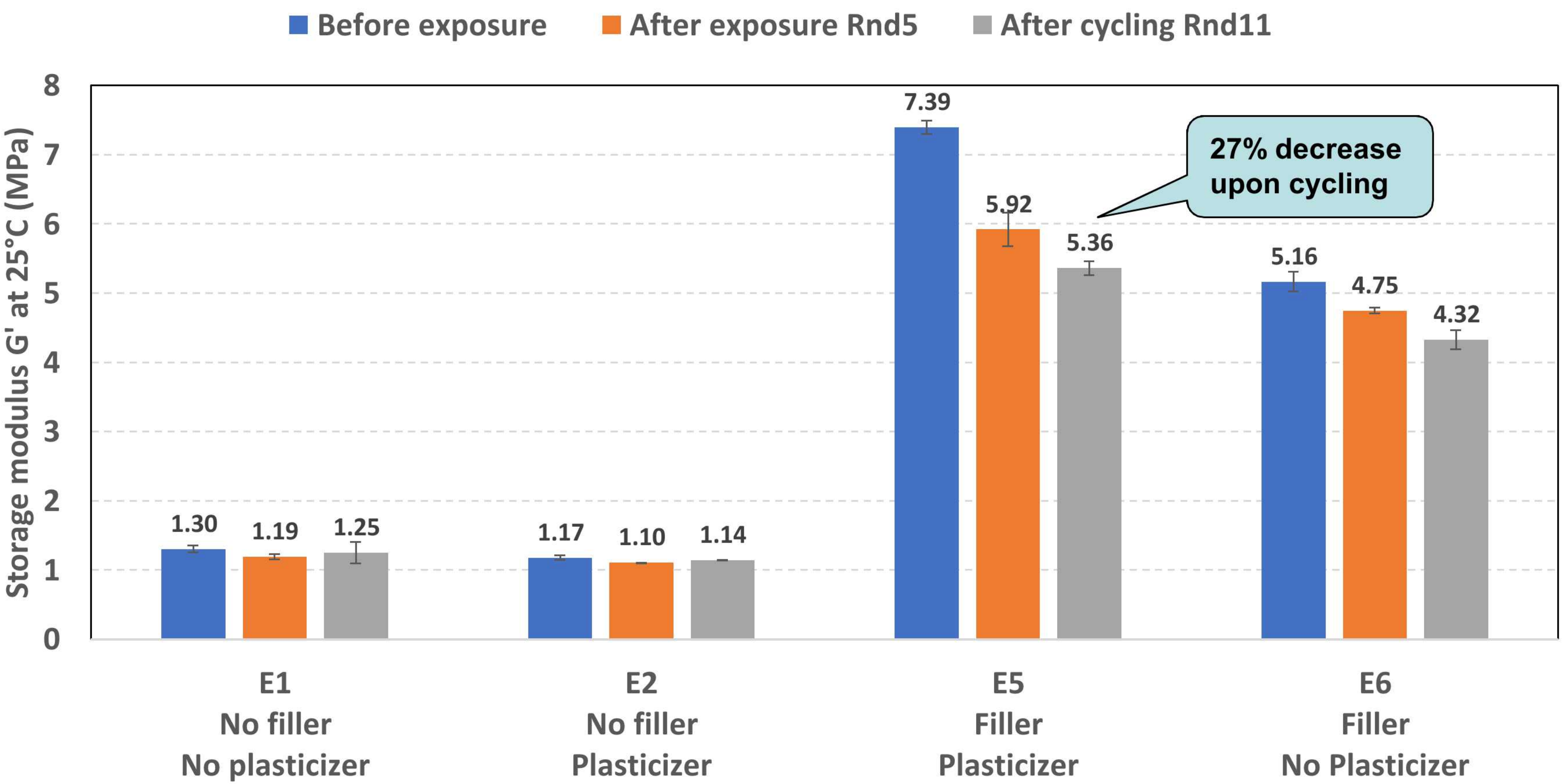


Compression set for E5 increases upon H2 exposure for both static and cycling modes – possible plasticization of matrix and/or retention of H_2 by fillers

EPDM Storage modulus: Cycling vs. static H_2 exposure

PNNL EPDM Formulations, effect of H2 exposure (Rnd 5) and H2 cycling (Rnd 11) on modulus

DMTA, 1 Hz, 5°C/min, average of two specimens



Significant change in storage modulus indicates possible plasticization of EPDM E5 (and E6) and influence due absorption/retention of H_2 by fillers

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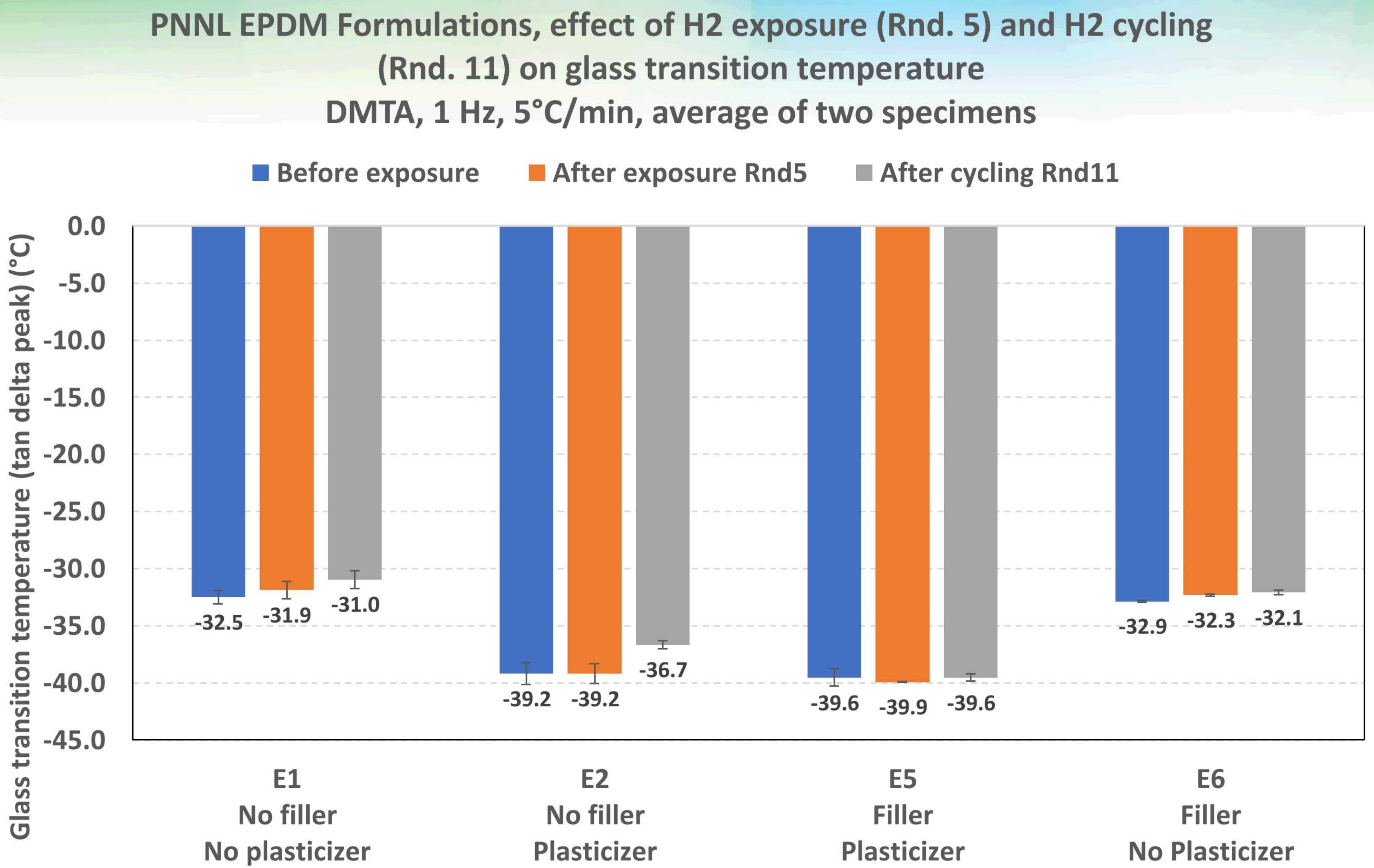
EPDM Glass transition temperature : Cycling vs. static H_2 exposure



Glass transition temperatures for E5 does not change – no change in crosslink density of polymer network

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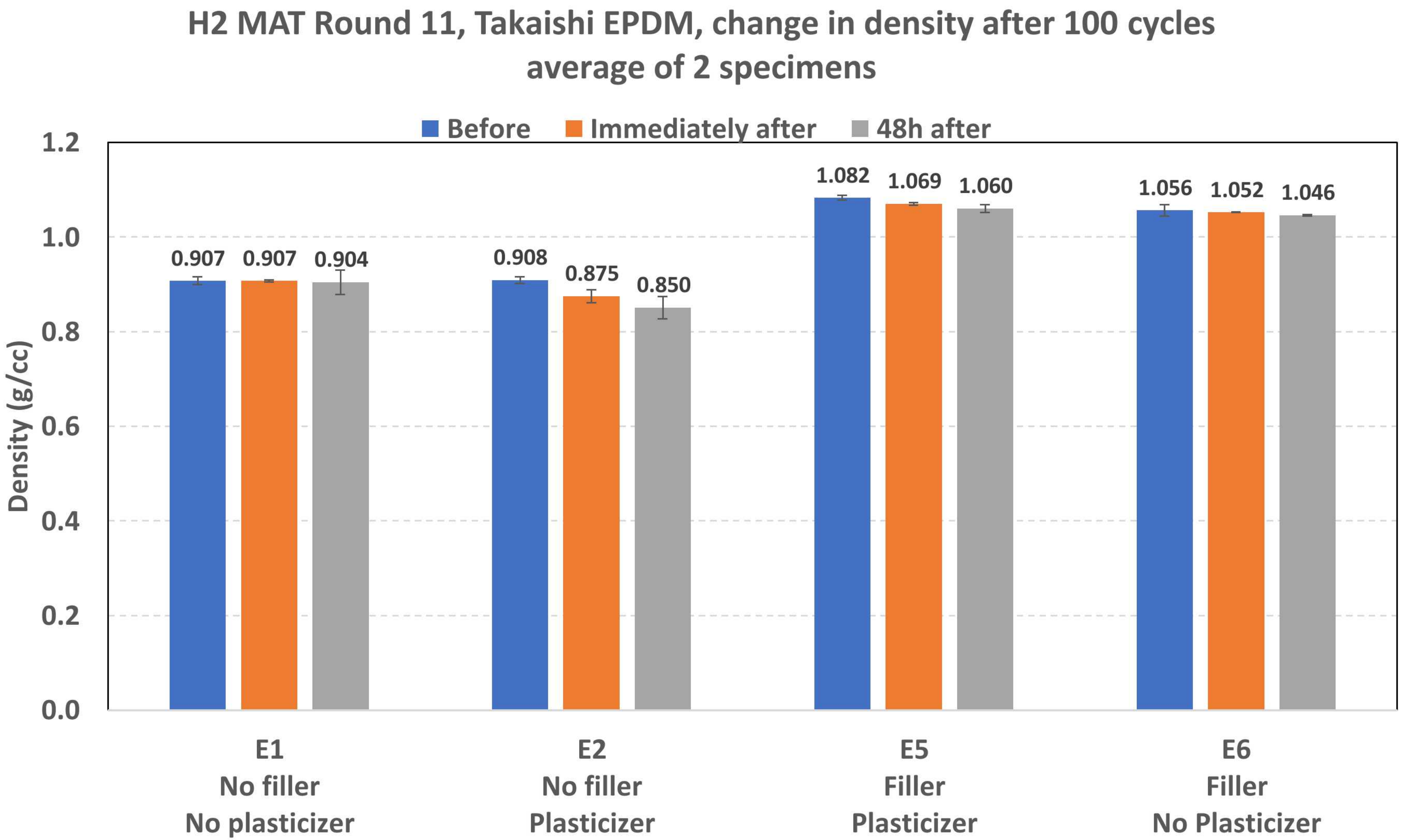
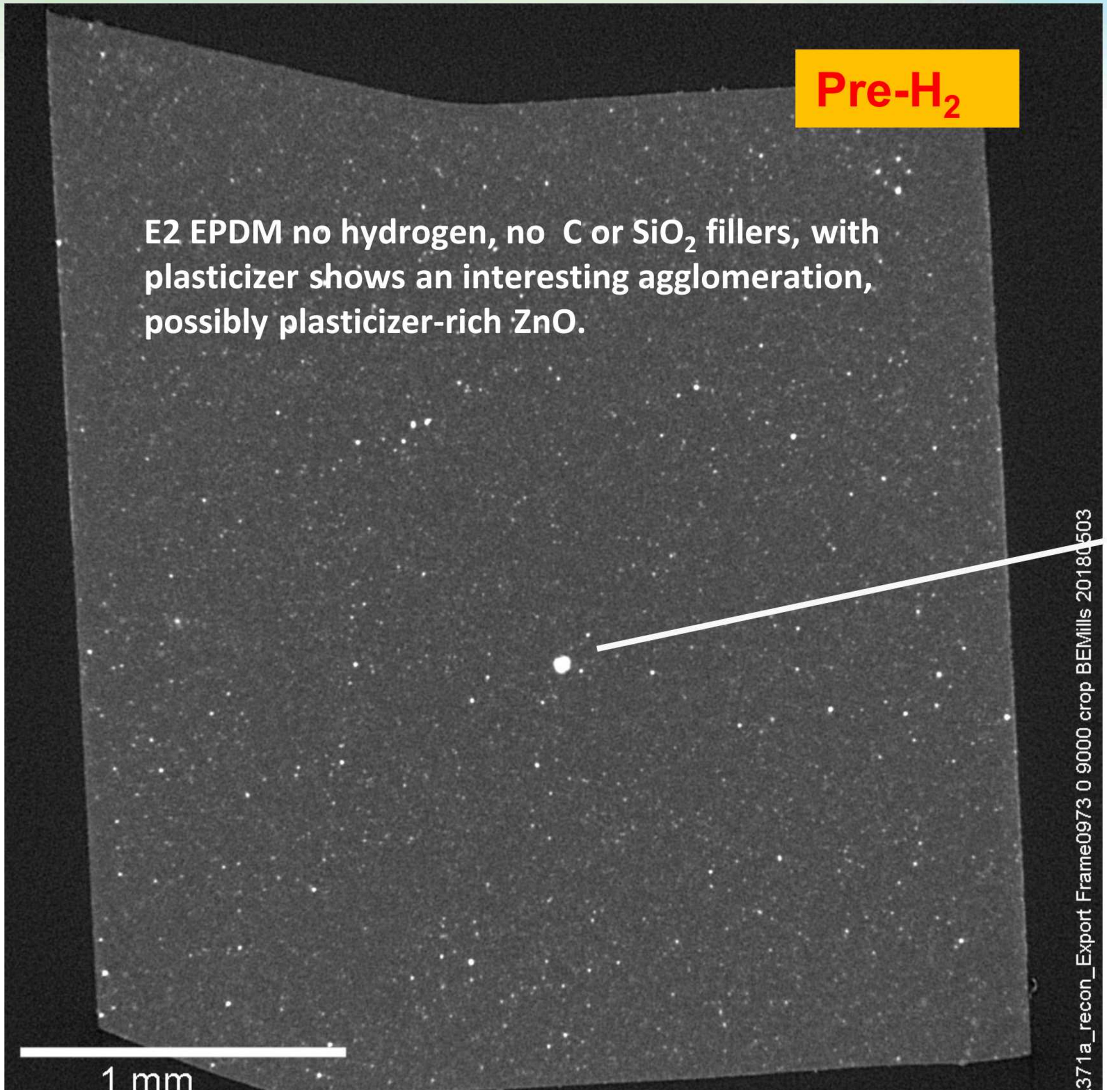
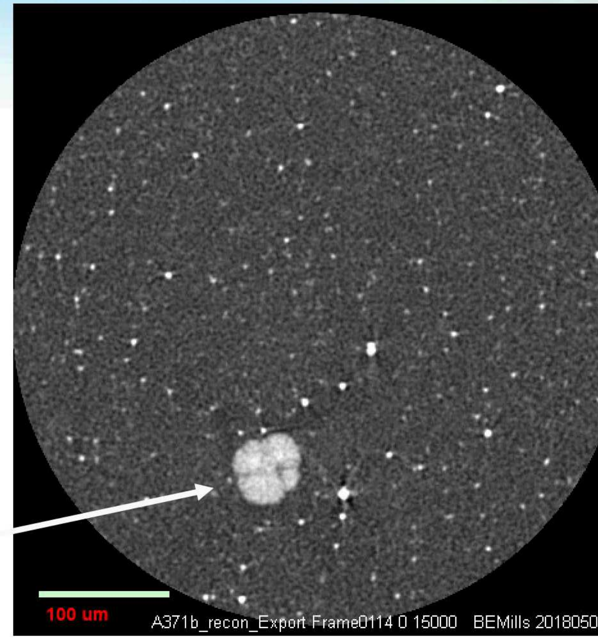
EPDM Density: cycling vs. static H_2 exposure



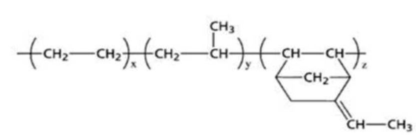
Densities of EPDM formulations change insignificantly upon H2 exposure – minimal physical swelling due to tight network, high crosslink density and less free volume

EPDM Micro CT: Compounding effects in E2, Pre-H_2

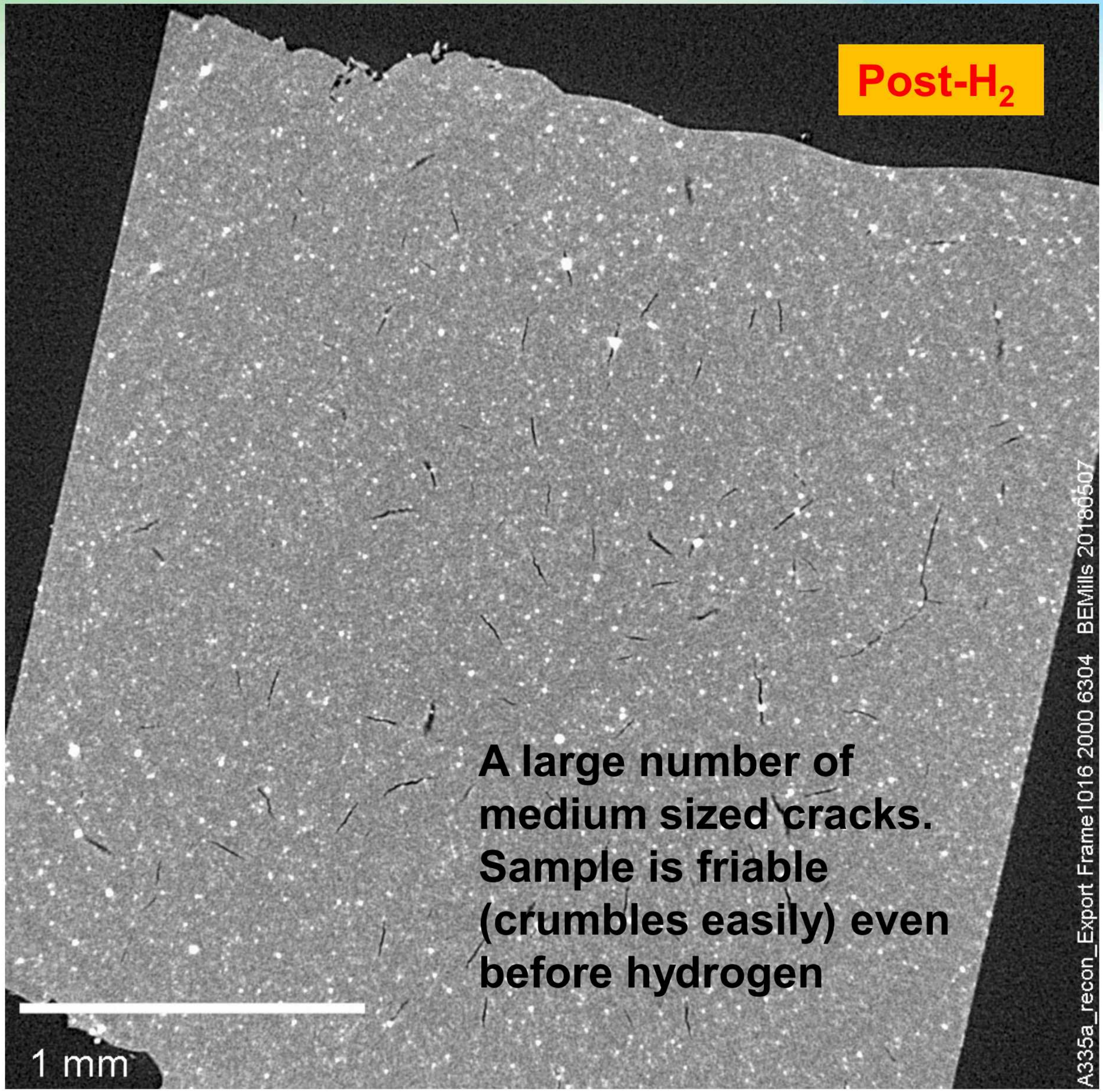




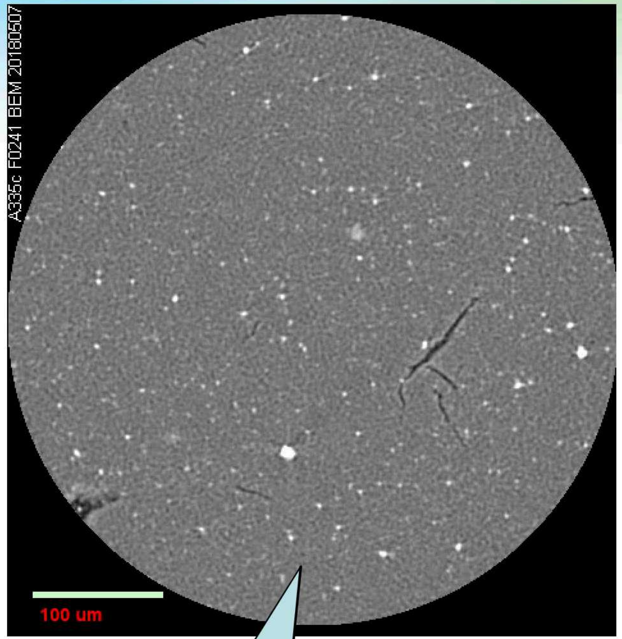
Compounding is critical to proper distribution of polymer additives



EPDM Micro CT: EPDM E1 (with no plasticizer and no C and SiO_2 filler)

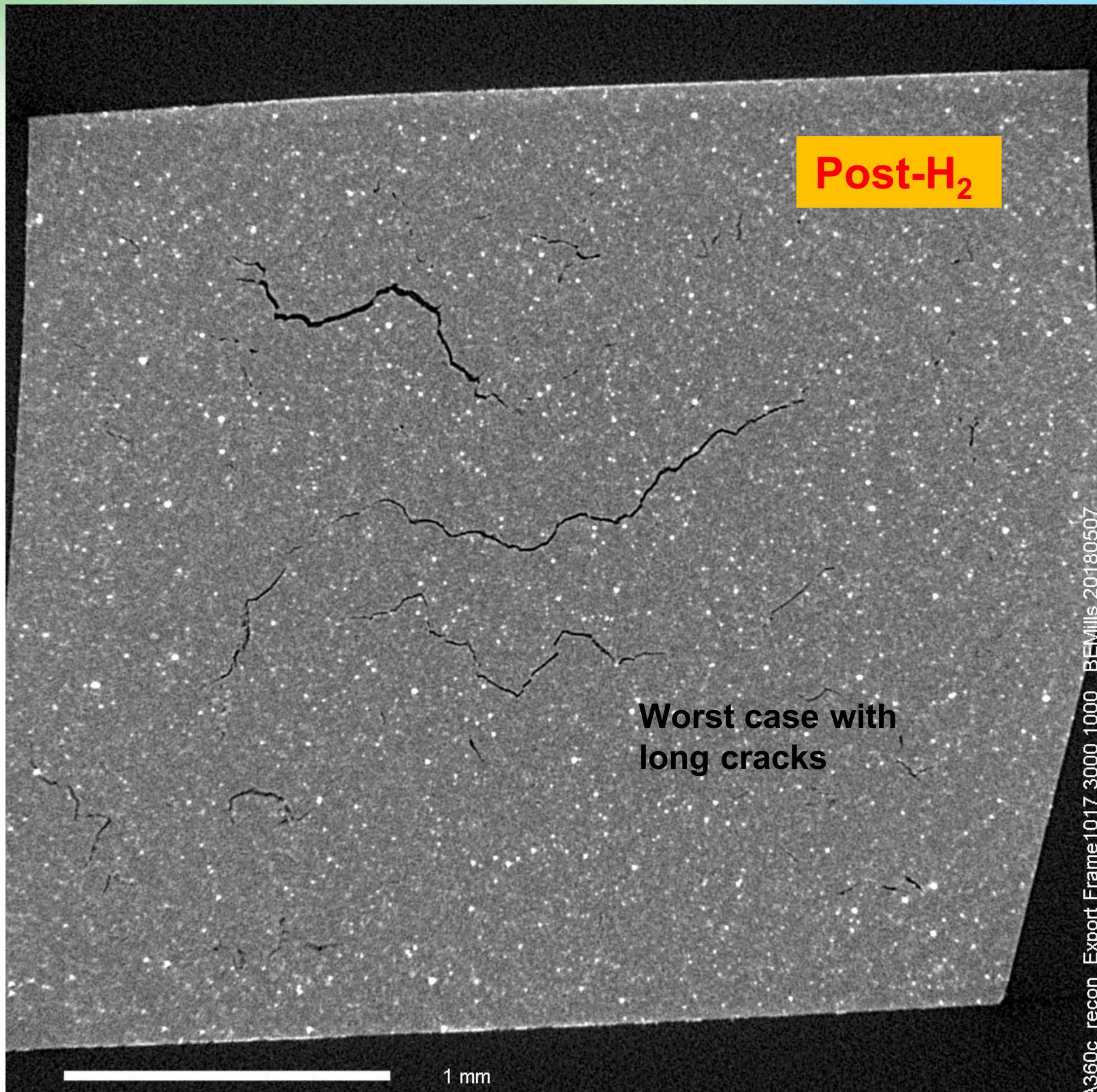


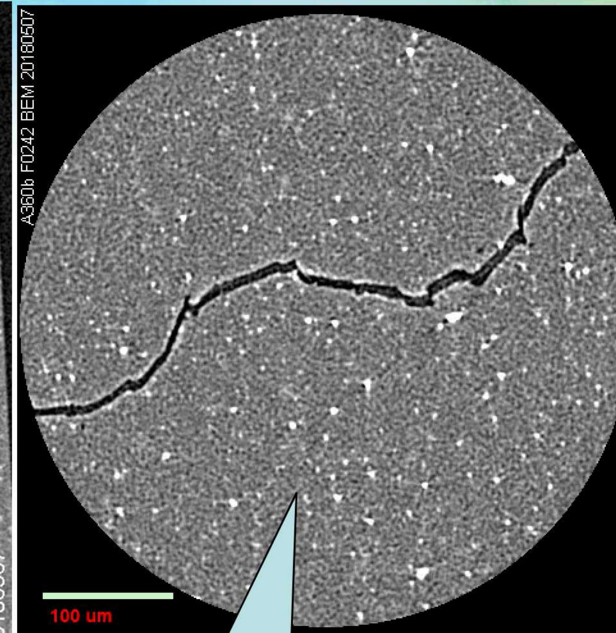
A large number of medium sized cracks. Sample is friable (crumbles easily) even before hydrogen



Patches, previously seen in E5 and E6 as possible lower Z agglomerates of ZnO and matrix, are not seen here

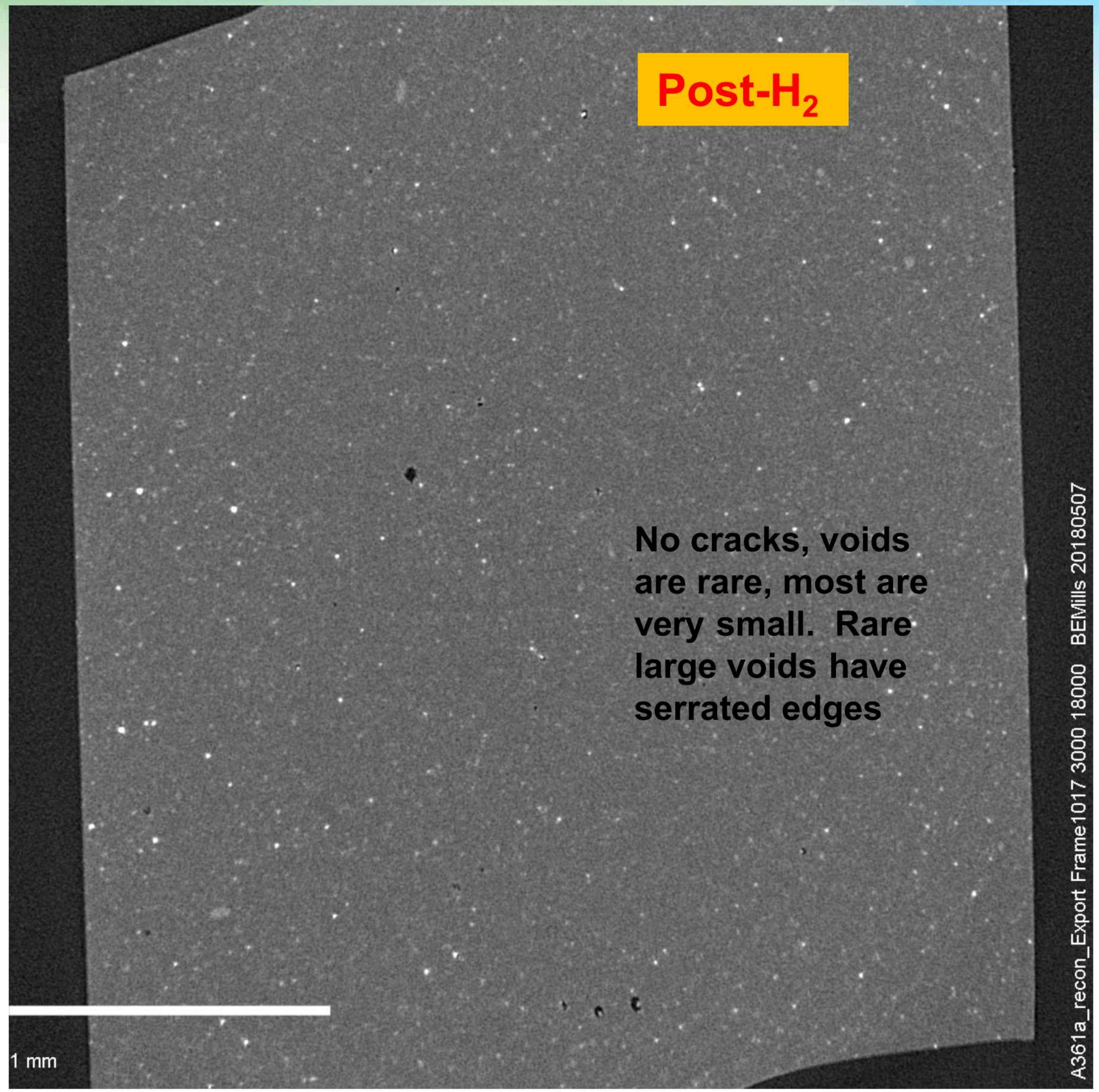
EPDM Micro CT: EPDM E2 (with plasticizer and no C, SiO_2 fillers)

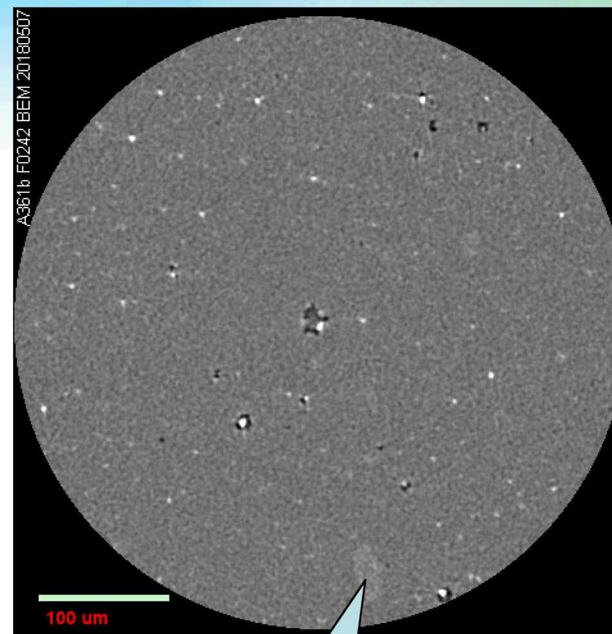




Patches, seen in unexposed EPDM E2 as possible lower Z agglomerates of ZnO and matrix, are not seen here

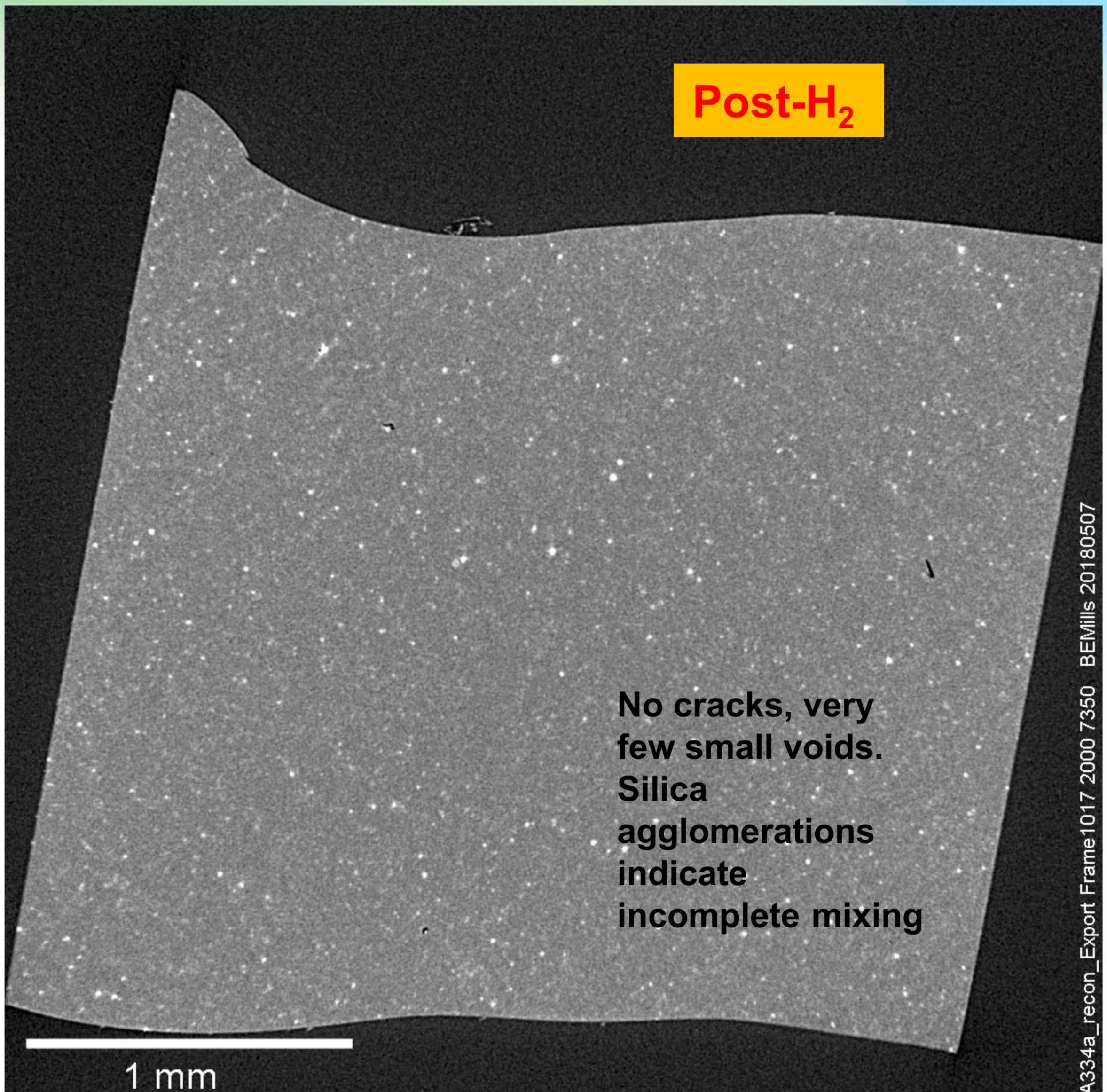
EPDM Micro CT: EPDM E5 (with C, SiO_2 fillers and plasticizer)

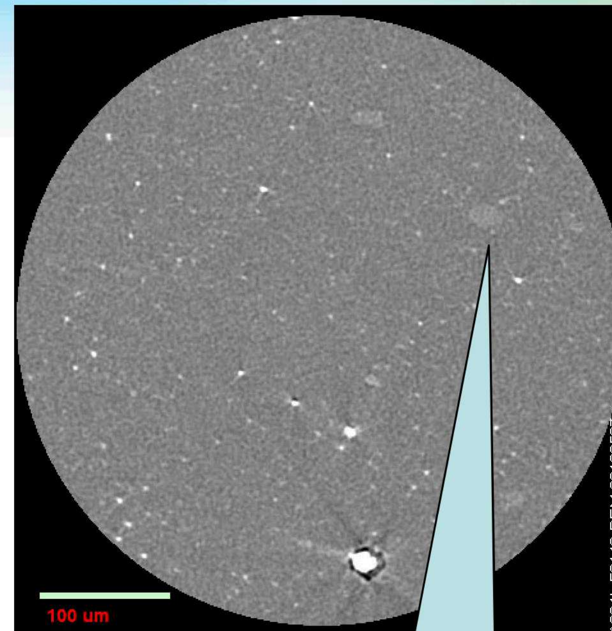




Several faint patches in the background which are possibly agglomerates of mostly silica and matrix

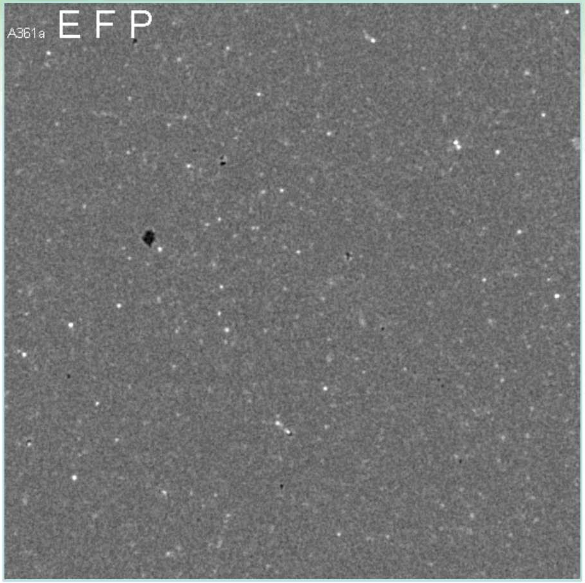
EPDM Micro CT: EPDM E6 (with C, SiO_2 fillers and no plasticizer)

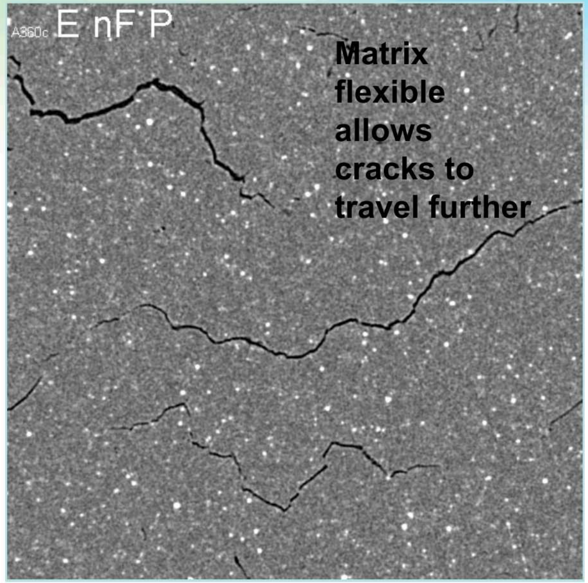




Several faint patches in the background of SiO_2 and matrix, as seen in E5

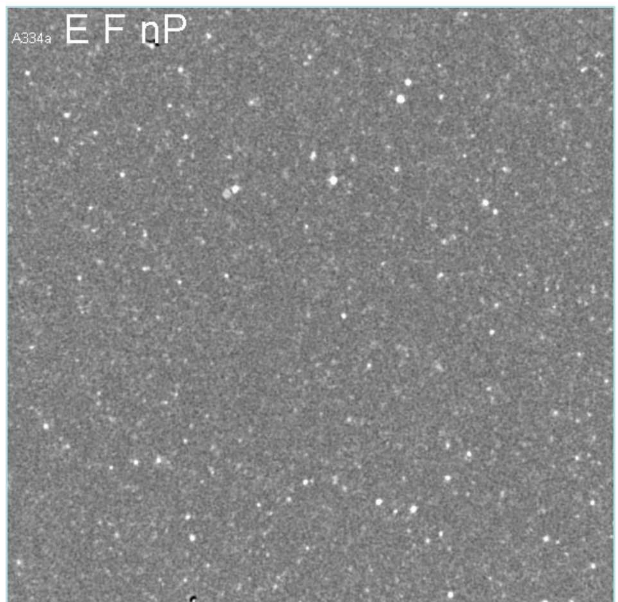
EPDM E1, E2, E5 and E6 after week-long static exposure of H_2

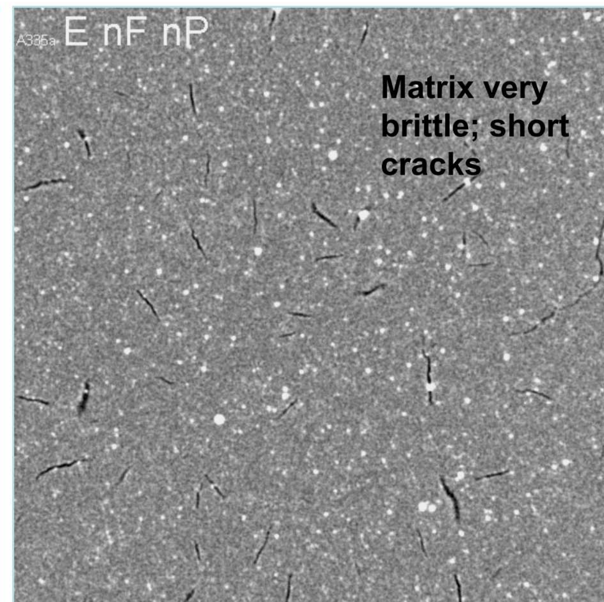




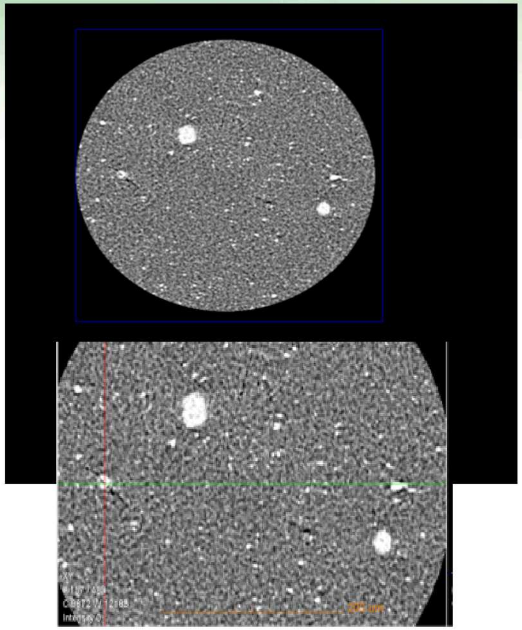
For custom EPDM formulations, presence of plasticizer changed the nature of cracks formed.

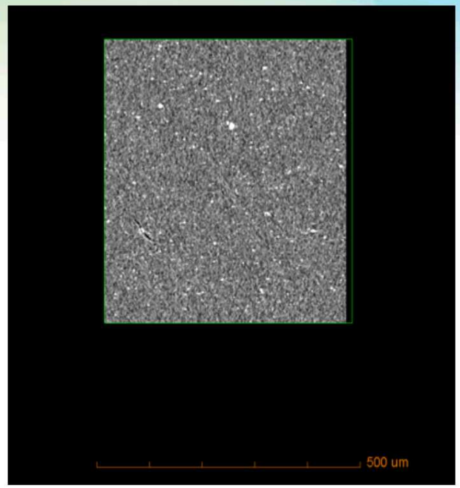
For custom EPDM formulations, addition of C and SiO_2 fillers helps mitigate crack formation.





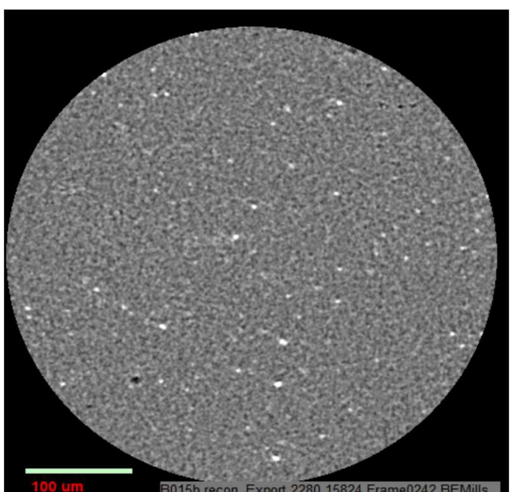
EPDM E1, E2, E5 and E6 after 100 cycles of H_2 exposure

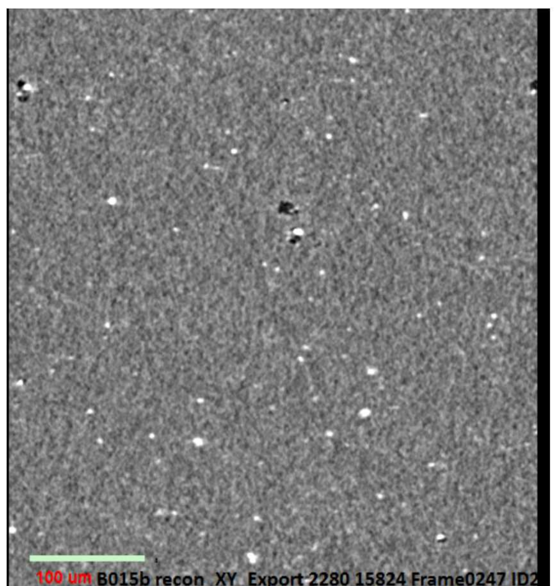




E1 (cycling) not much damage, small cracks around ZnO particles: different from E1 (static) which had numerous short cracks spread throughout the sample

Was time of exposure to high pressure more critical than static/cycling?

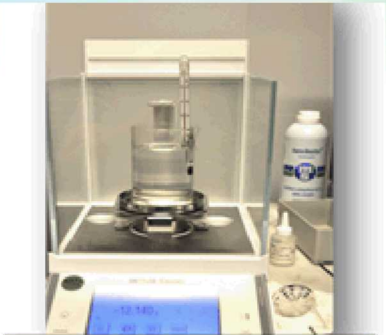




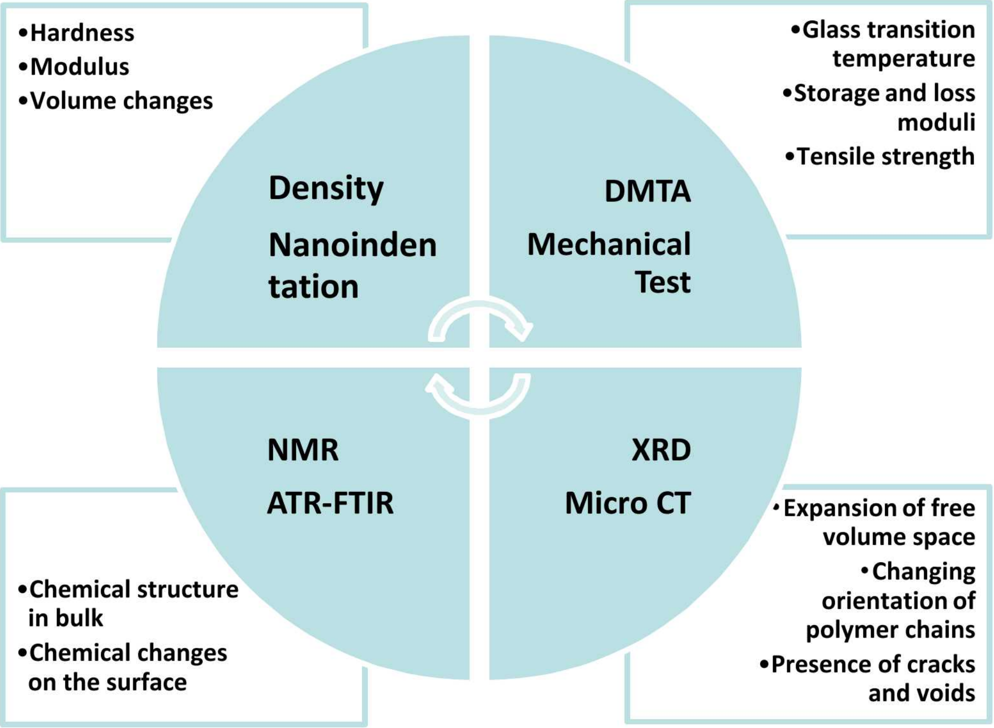
E6 Some cracks and voids (many) in the center and edge, long (150 microns), thin cracks that do not prefer any orientation; different from E6 in static which was crack-free

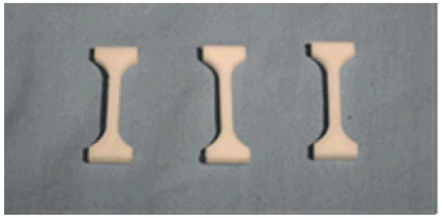
Thermoplastics (POM, PTFE, Nylon 6,6, PEEK, Nylon 11, HDPE) Test Conditions, Ex-situ Characterization techniques

1. One week-long static high pressure (100 MPa) @ ambient temperature (Rounds 1 & 2); Data only available for POM, PTFE, Nylon 11 and HDPE
2. 100 cycles, 86 MPa to 17 MPa and back, ambient temperature, rate of pressurization = 13.79 MPa/min; rate of depressurization = 2.29 MPa/min (Rounds 9 & 10)



Density measurements set-up





Micro-tensile specimens

Micro CT specimen of POM mounted and ready for imaging

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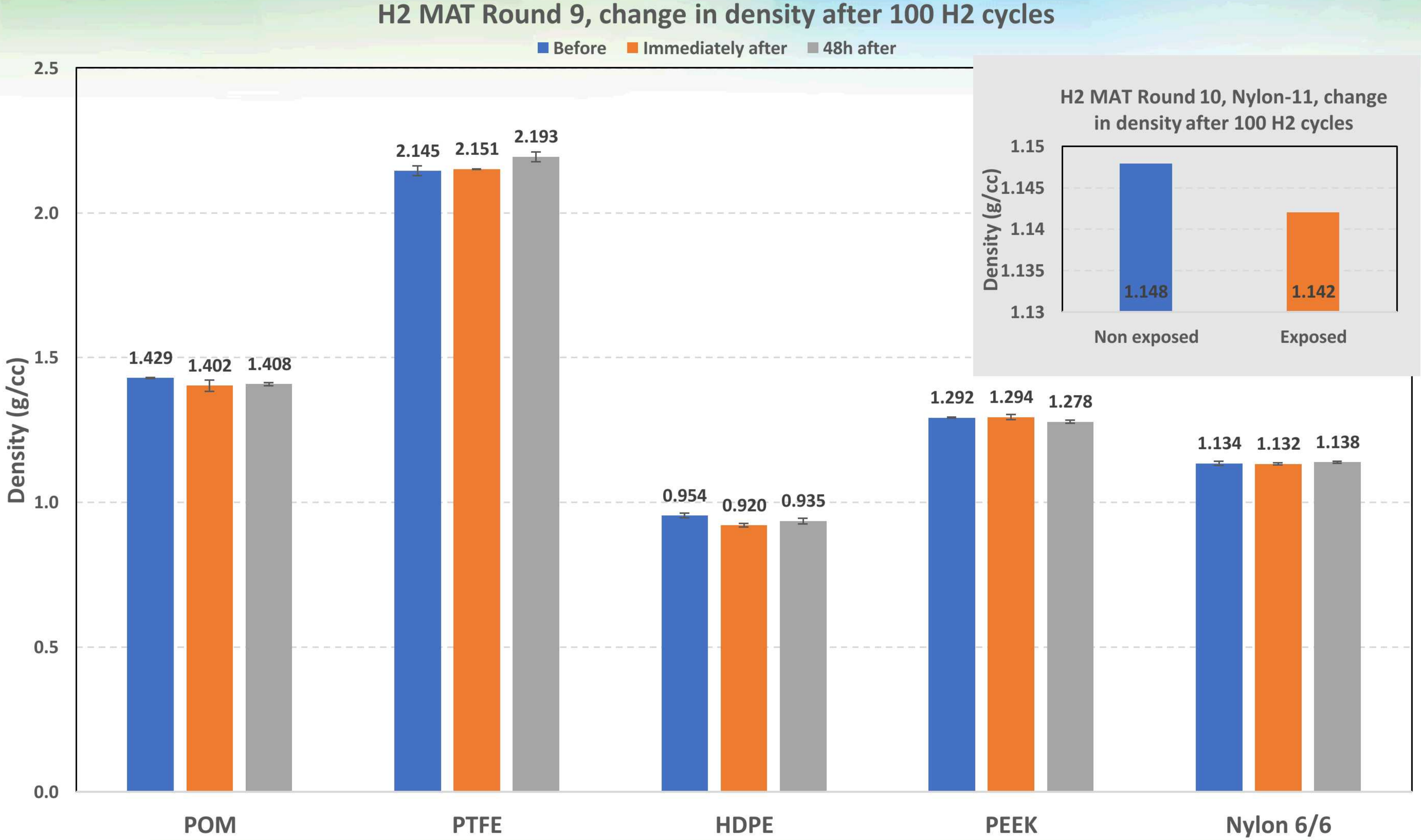
Density changes in thermoplastics: 100 cycles in H2

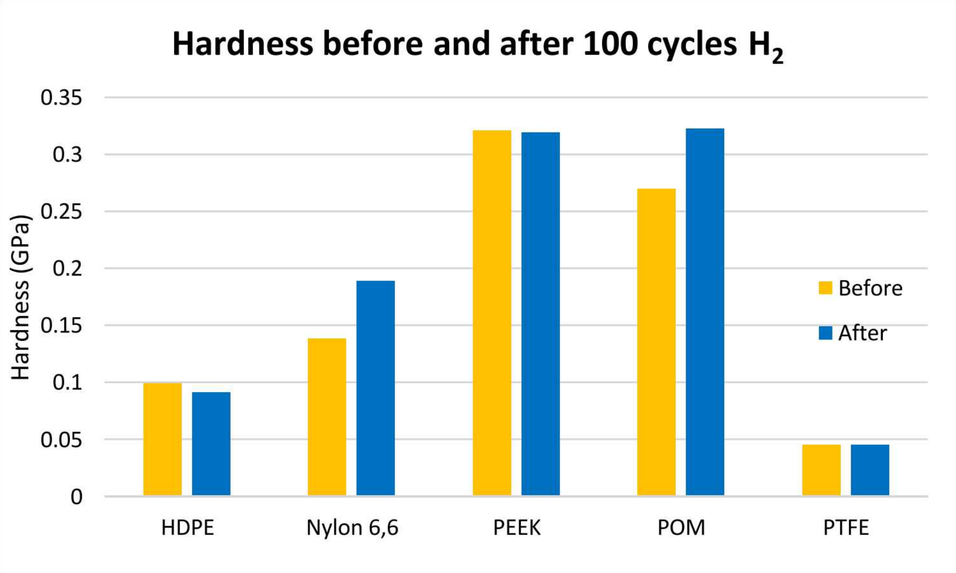


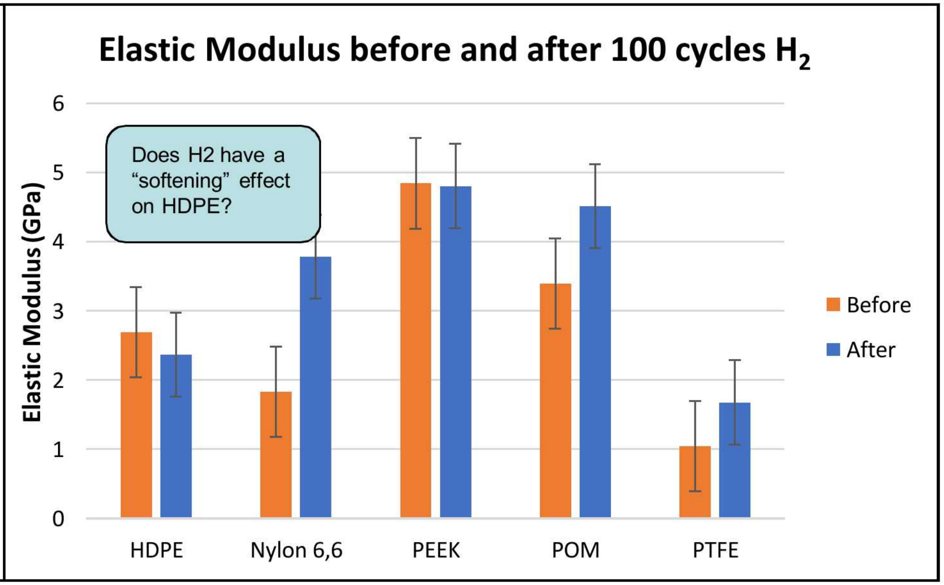
Thermoplastics do not show significant swelling as elastomers in H_2

Nanoindentation of thermoplastics: 100 cycles of H_2

SAMPLE ID	Hardness (GPa)	Post Hardness (GPa)	Modulus (GPa)	Post Modulus (GPa)
HDPE	0.0989 ± 0.0082	0.091385 ± 0.00314	2.6916 ± 0.1267	2.364575 ± 0.04735
Nylon 6-6	0.1382 ± 0.0096	0.188941 ± 0.01226	1.8335 ± 0.1721	3.783291 ± 0.16664
PEEK	0.3211 ± 0.0099	0.31945 ± 0.03074	4.8409 ± 0.0898	4.802973 ± 0.08113
POM	0.2699 ± 0.0282	0.32283 ± 0.021764	3.3937 ± 0.1885	4.510542 ± 0.16498
PTFE	0.0452 ± 0.0061	0.04506 ± 0.007376	1.0476 ± 0.2192	1.676048 ± 0.22044

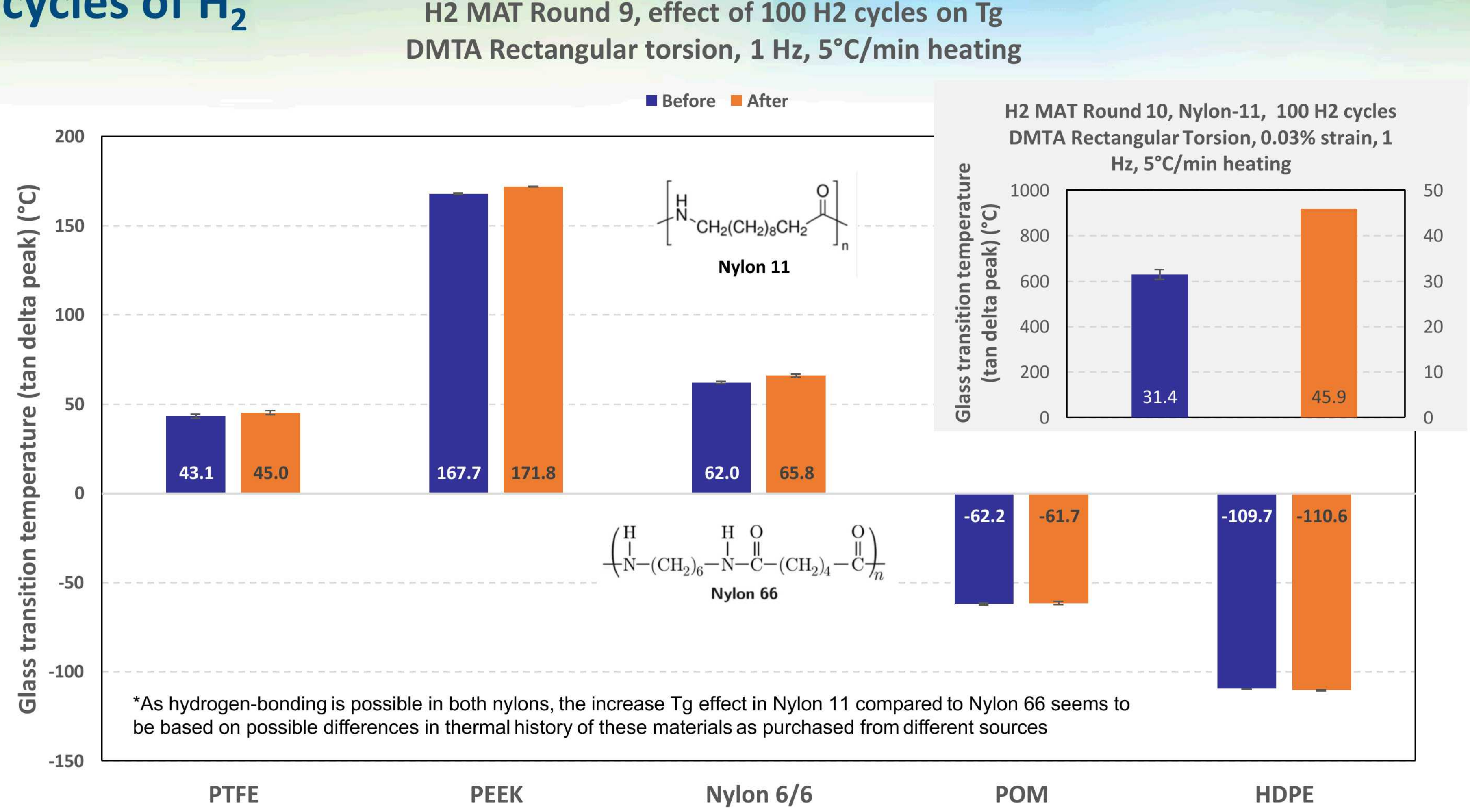
- **HDPE reduces in both hardness and modulus**
- **PEEK does not change in hardness and modulus**
- **PTFE does not change in hardness but, increases in modulus**





H_2- exposed Nylon, POM show a higher hardness, PEEK and PTFE are unchanged and HDPE shows a small decrease

DMTA of thermoplastics (Glass transition temperature T_g): 100 cycles of H_2



T_g changes due to H_2 exposure and hence, related microstructural effects are minimal for plastics tested except for the 46% increase seen for Nylon 11*

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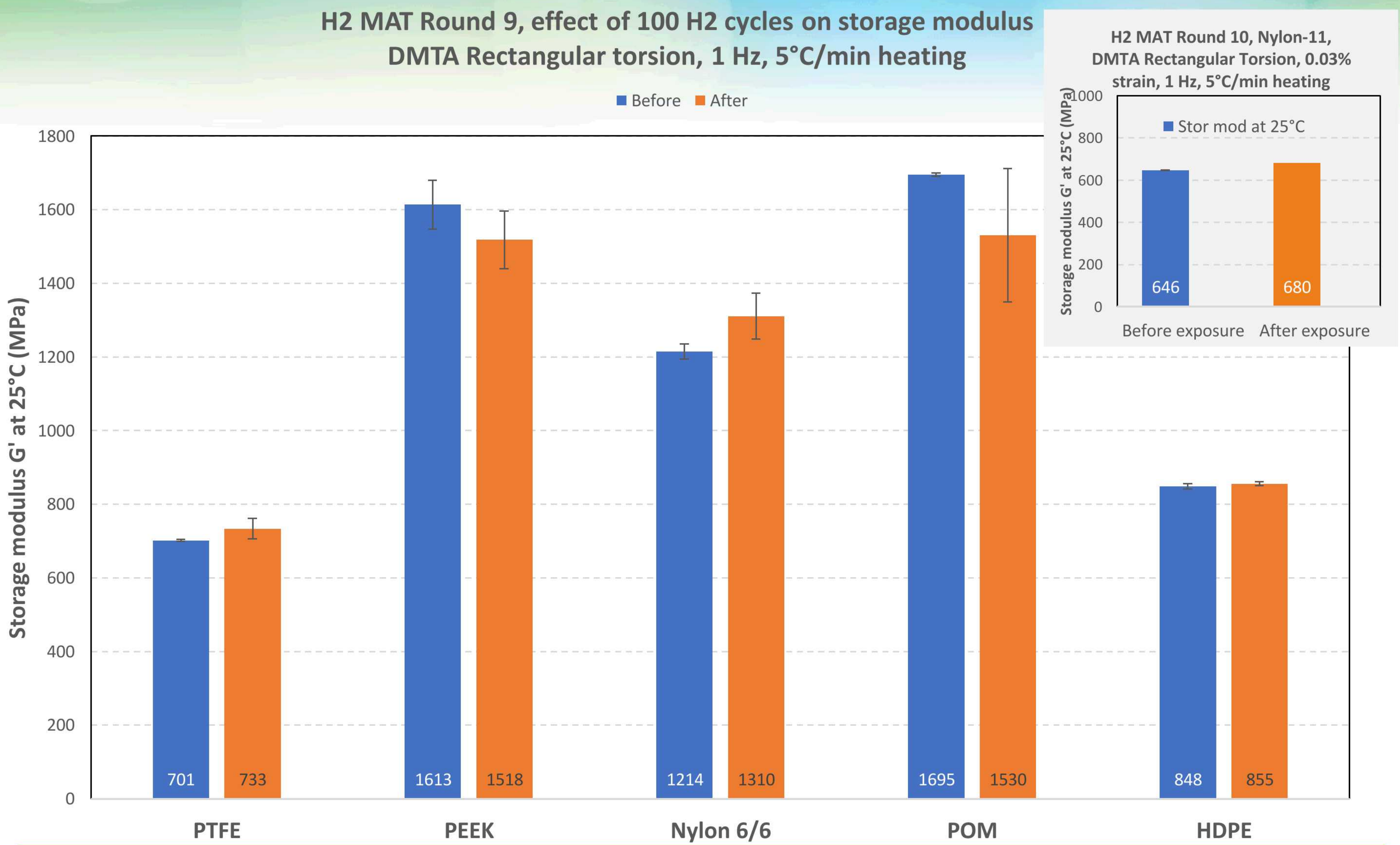
DMTA of thermoplastics (Storage modulus): 100 cycles of H_2



No significant change in storage modulus (bulk property) for all plastics tested. H2 interactions in these materials does not affect their ability to store energy elastically.

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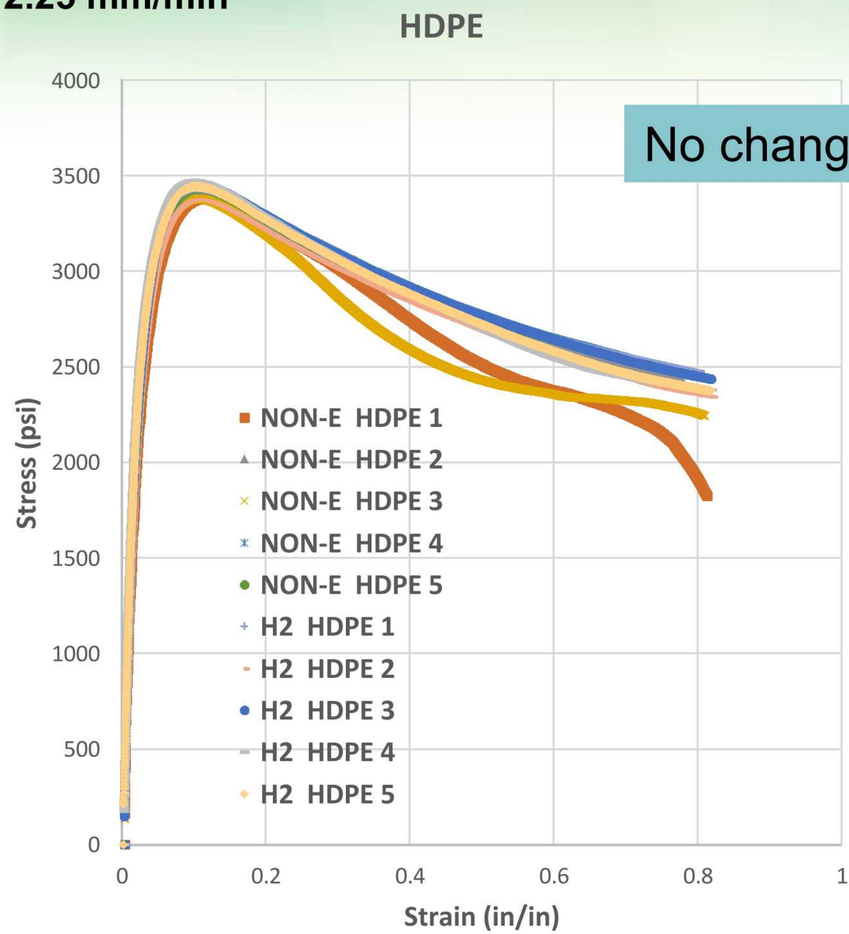
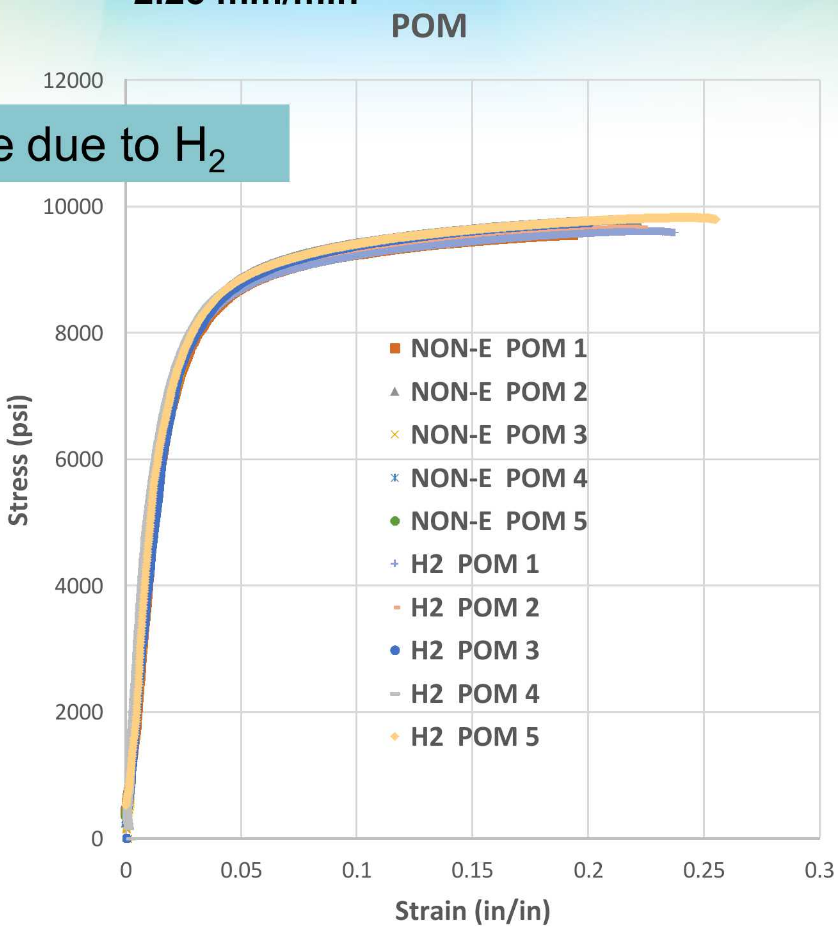
Mechanical testing of thermoplastics (micro tensile): 100 cycles of H_2

No change due to H_2

2.25 mm/min



2.25 mm/min



Sample	Yield stress (psi)	Modulus (ksi)	Strength (psi)	Elongation (percent)
NE HDPE	2182±33	111.1±8.2	3412±26	79.28±1.71
E HDPE	2286±46	115.6±4.5	3438±34	81.74±0.44

Sample	Yield stress (psi)	Modulus (ksi)	Strength (psi)	Elongation (percent)
NE POM	6384±136	428.6±21.1	9660±79	19.82±1.50
E POM	6288±190	460.0±39.9	9744±89	22.99±1.79

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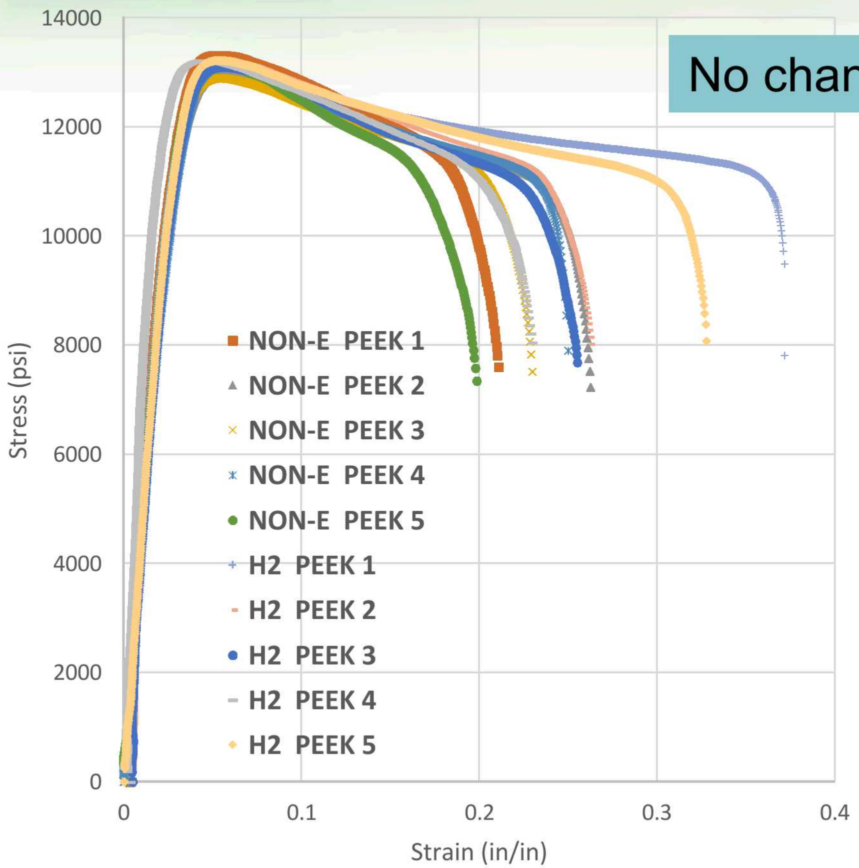
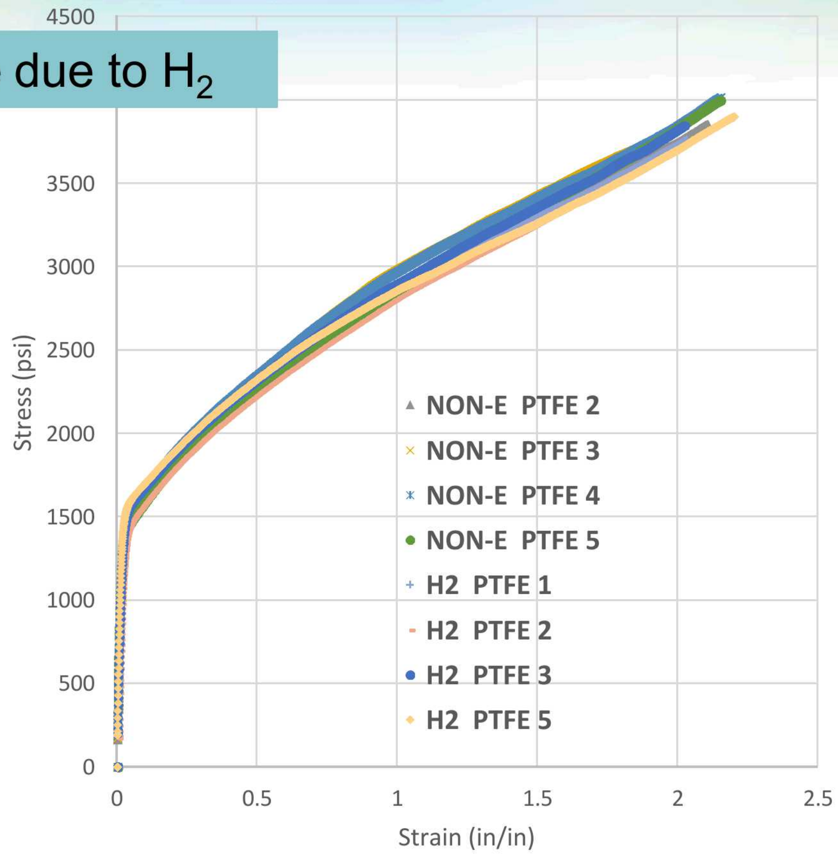
Mechanical testing of thermoplastics (micro tensile): 100 cycles of H_2

No change due to H_2

2.25 mm/min PEEK



9.0 mm/min PTFE



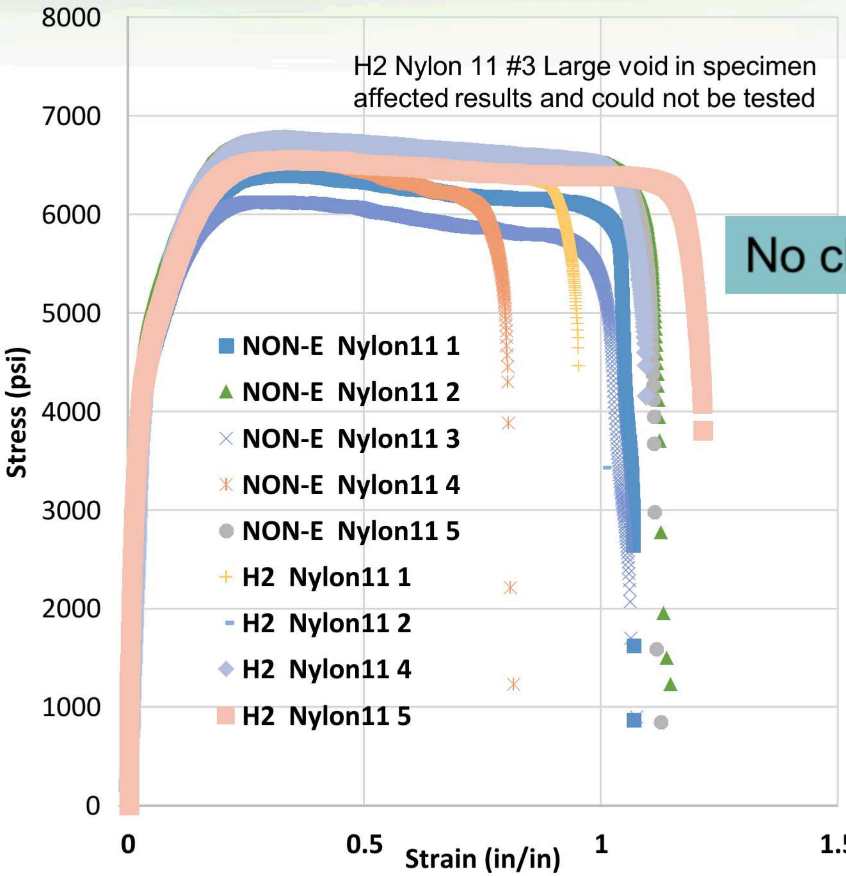
Sample	Yield stress (psi)	Modulus (ksi)	Strength (psi)	Elongation (percent)
NE PEEK	10813±188	420.9±18.1	13093±149	23.06±2.38
E PEEK	11038±141	468.4±91.3	13199±54	28.96±5.23

Sample	Yield stress (psi)	Modulus (ksi)	Strength (psi)	Elongation (percent)
NE PTFE	1266±21	66.1±5.8	3898±122	207.12±11.82
E PTFE	1261±68	71.8±12.1	3775±89	206.57±8.05

Mechanical testing of thermoplastics (micro tensile): 100 cycles of H_2

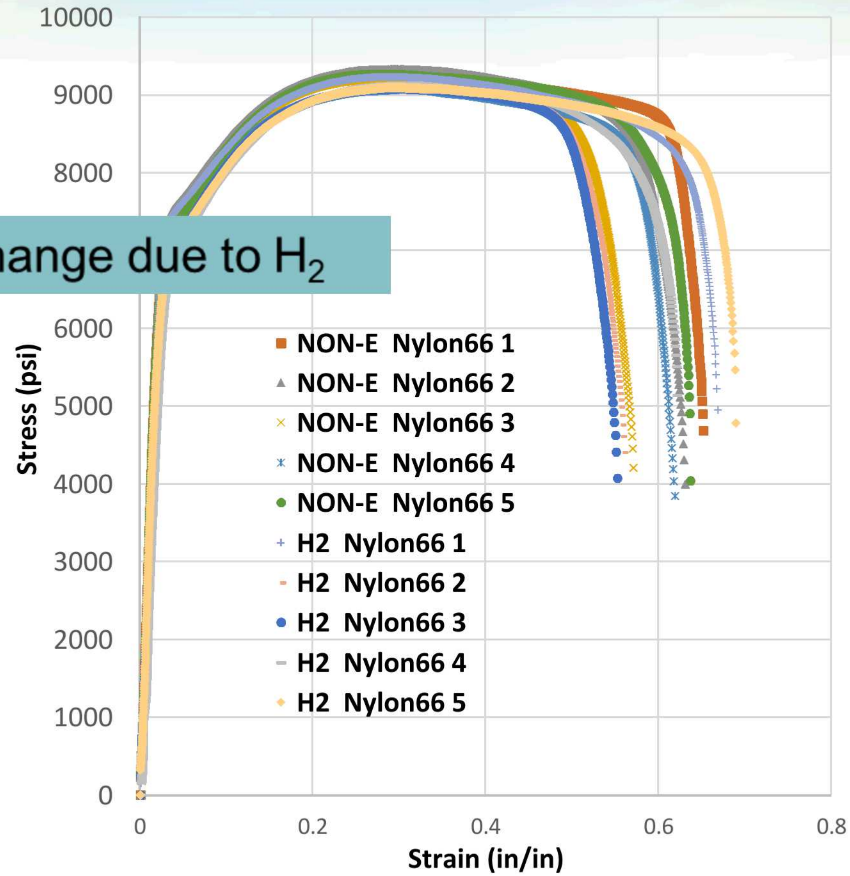
2.25 mm/min

Nylon 11



2.25 mm/min

Nylon66

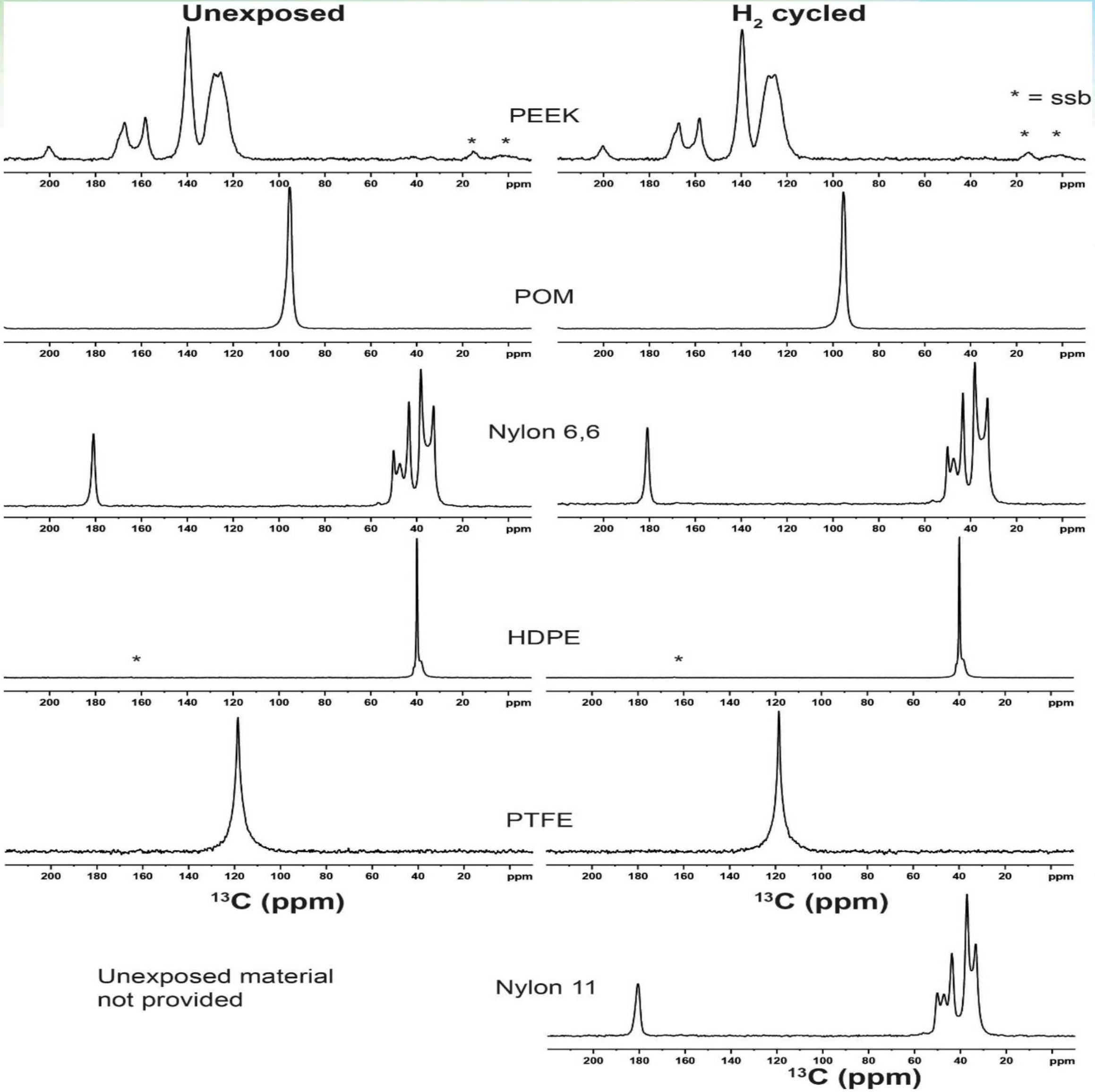


No change due to H_2

Sample	Yield stress (psi)	Modulus (ksi)	Strength (psi)	Elongation (percent)
NE Nylon 11	3653±158	166.1±13.0	6528±241	104.63±11.92
E Nylon 11	3779±228	151.4±18.7	6654±18.7	108.22±9.38

Sample	Yield stress (psi)	Modulus (ksi)	Strength (psi)	Elongation (percent)
NE Nylon 66	6358±168	303.7±12.9	9225±86	62.15±2.77
E Nylon 66	6101±251	284.4±13.8	9133±58	61.79±5.56

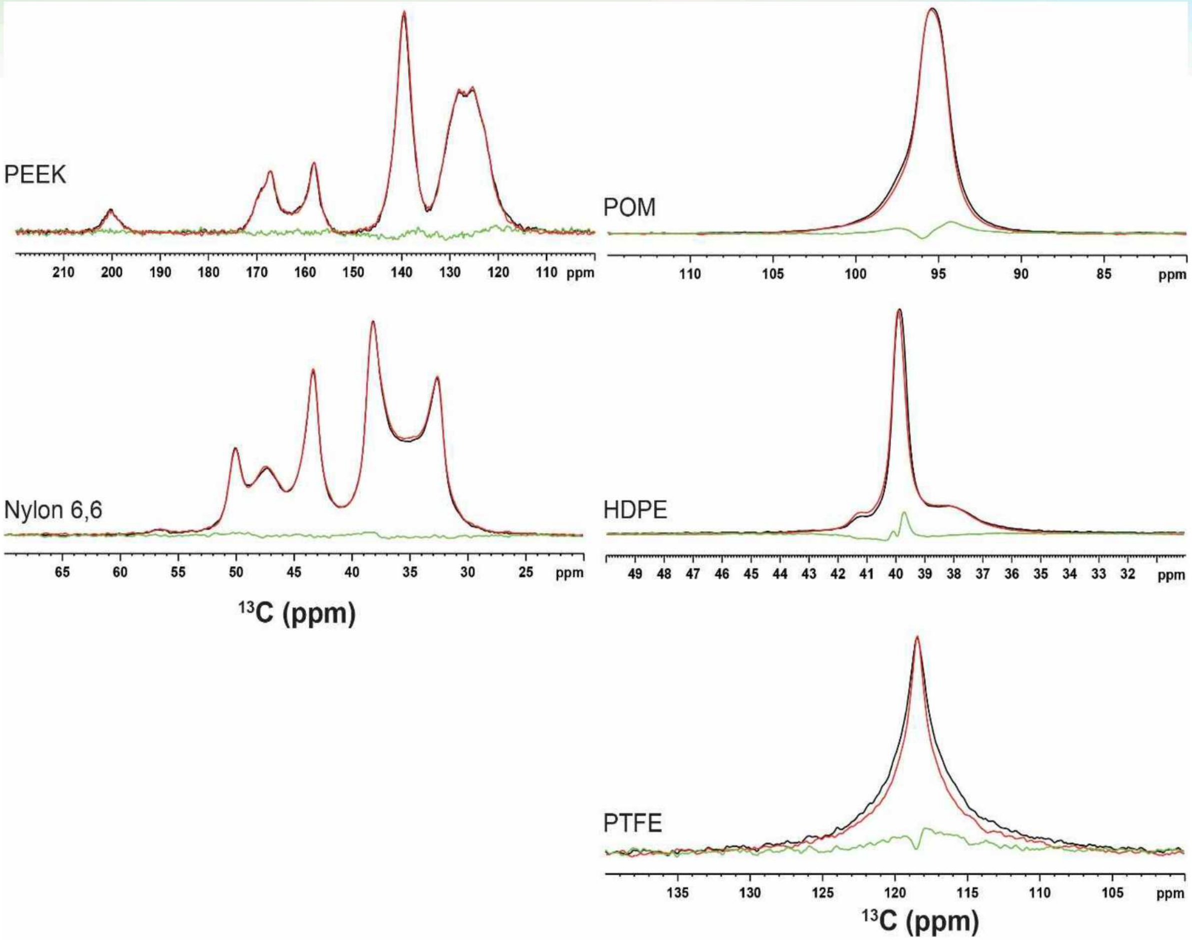
Solid state ^{13}C CPMAS NMR: 100 cycles of H_2



Solid state ^{13}C CPMAS NMR of unexposed and exposed polymer materials

- While ^{13}C NMR would not be reveal H_2 gas (no Carbon), any significant degradation or reaction by products might be observable.
- For these materials there are *no C-containing reaction* products for any of the materials - H_2 cycling has not caused any polymer degradation.

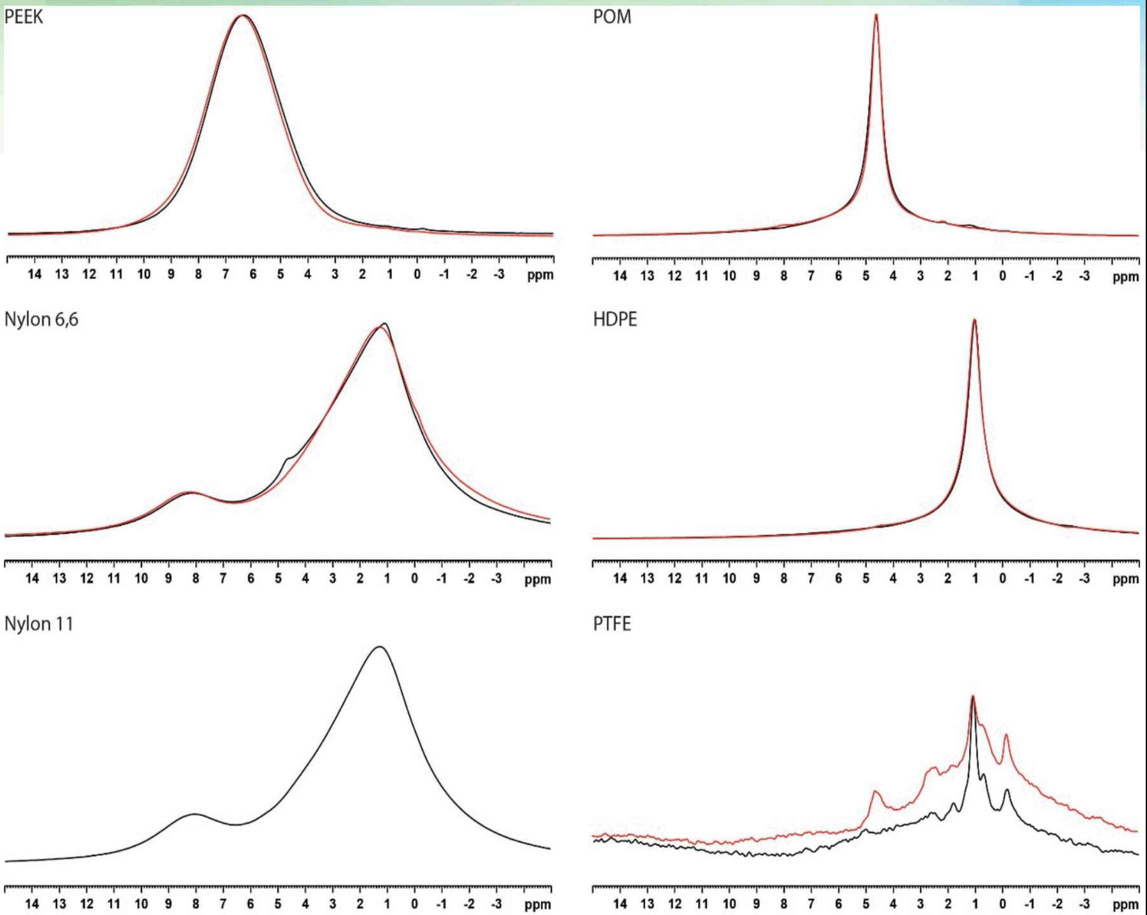
Solid State ^{13}C CPMAS NMR of thermoplastics: 100 cycles of H_2



Solid state ^{13}C CPMAS NMR of different polymer materials - changes in morphology related expansion. Black (unexposed), red exposed and green (difference).

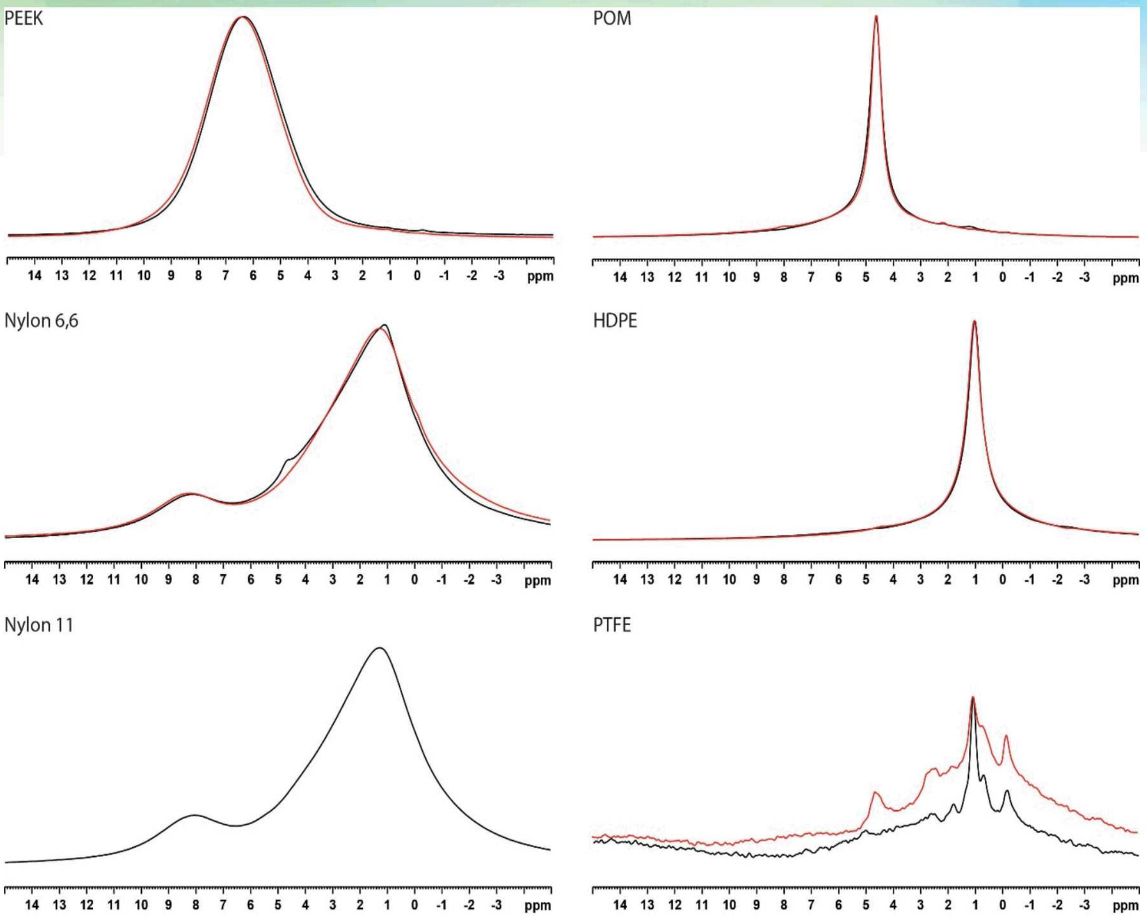
- The PEEK and Nylon 6,6 polymer revealed no differences due to exposure.
- Both the POM and PTFE polymer revealed a *minor* decrease in the line width (most notably in the PTFE) suggesting an increase in the mobile (amorphous fraction) for those polymers.
- The HDPE polymer also revealed some variation following exposure demonstrating small changes in the chain conformations for this polymer with exposure.
- All these changes are considered minor but may show up in subtle changes of the DMA analysis.

Solid State ^{1}H MAS NMR of thermoplastics: 100 cycles of H_2



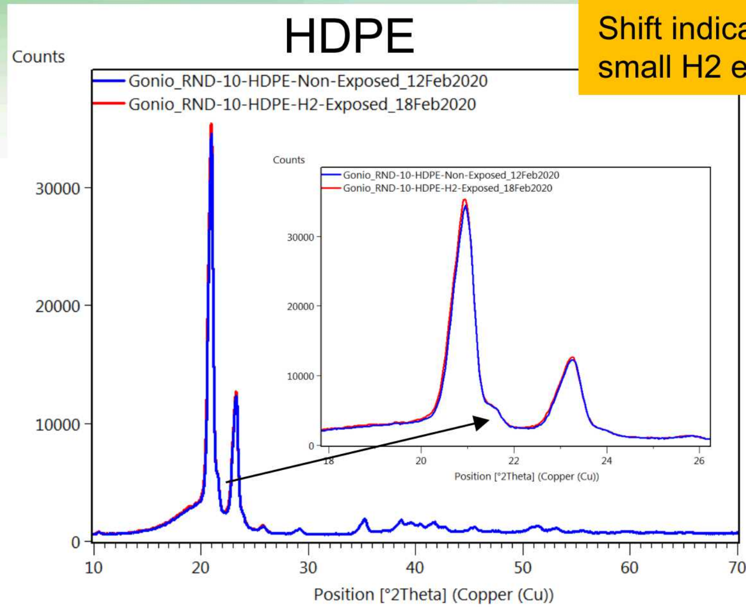
- ^{1}H NMR chemical shifts experimentally observed for these materials have resonances consistent with the H in the different materials
- In the case of PEEK (aromatic H), Nylon 6,6 and Nylon 11 (NH and CH_2 protons) are broad due to these materials being more rigid, while POM and HDPE show a single narrow resonance arising from the methylene environment
- There is not clear resonance observed corresponding to H_2 gas absorbed into these polymers, suggesting that if present the concentration is *very low*.
- The Nylon 6,6 has a small resonance at δ = 4.8 ppm, but this is present ONLY in the un-exposed material and is assigned to absorbed water (common for Nylons).
- There is a minor resonance at δ = 4.3 ppm that grows in with exposure in the PTFE.

Solid State [1]H MAS NMR of thermoplastics: 100 cycles of H_2

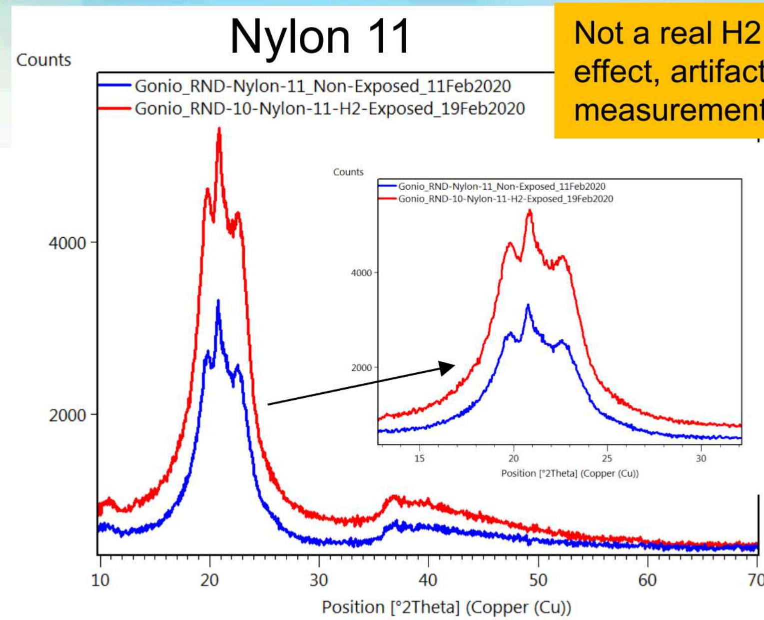


- One of the difficulties is attempting to see minor H environments in a sea of H originating from the virgin polymer.
- One of the methods used in the past to explore minor species is a spin -spin relaxation T_2 filtered ^{1}H MAS NMR spectra as shown. This filtering will retain ONLY mobile species present in the polymers. These resonances could represent impurities, additives, mole release agents or highly amorphous mobile regions.
- It was argued that H_2 gas (if present) would be mobile and narrow and retained during this T_2 filtering. There is *NO apparent* H_2 gas detected in these T_2 filtered spectra.
- What was noted was that in some situations some of these minor mobiles disappeared with H_2 cycling. In particular, the Nylon 6,6, where the species at δ ~ 1 ppm and 4.8 ppm have almost completely disappeared with exposure. The resonance at $\delta = 4.8$ was previously assigned to water and was removed with H_2 exposure.
- The $\delta = 1$ ppm is a mobile alkyl proton environment (perhaps an impurity) has also been removed.

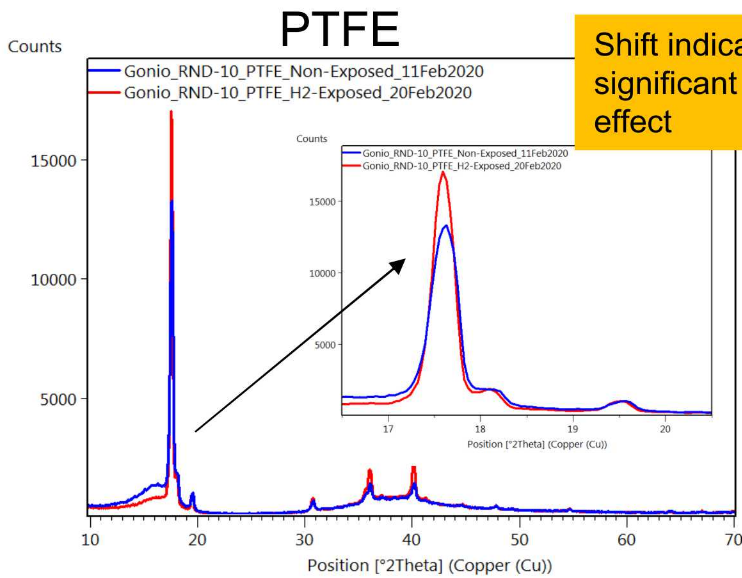
XRD of thermoplastics: 100 cycles of H_2



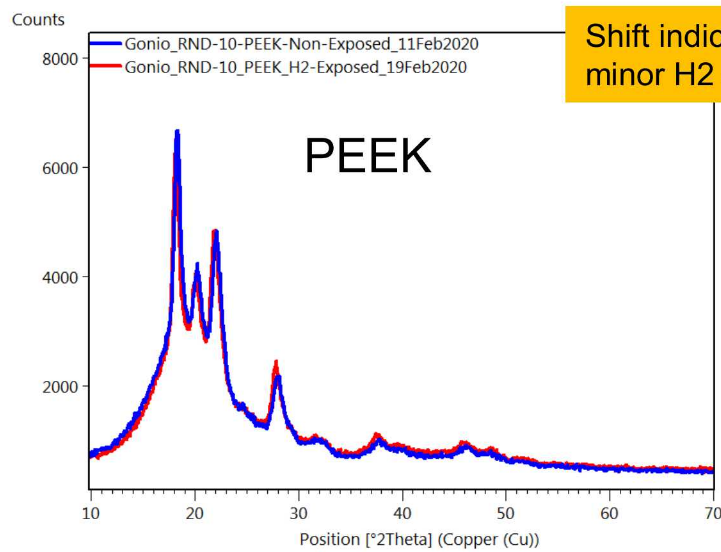
Shift indicates a small H2 effect



Not a real H2 effect, artifact of measurement



Shift indicates a significant H2 effect



Shift indicates a minor H2 effect

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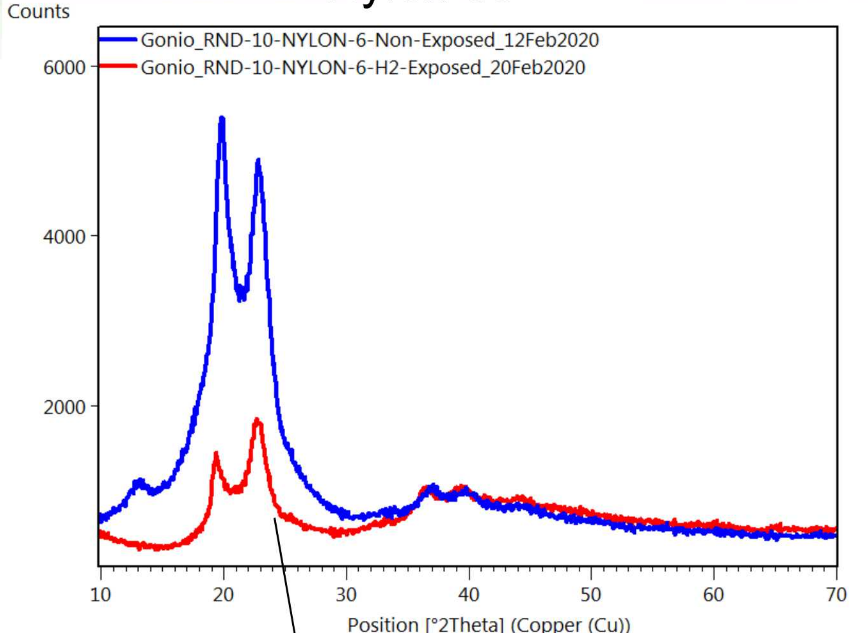
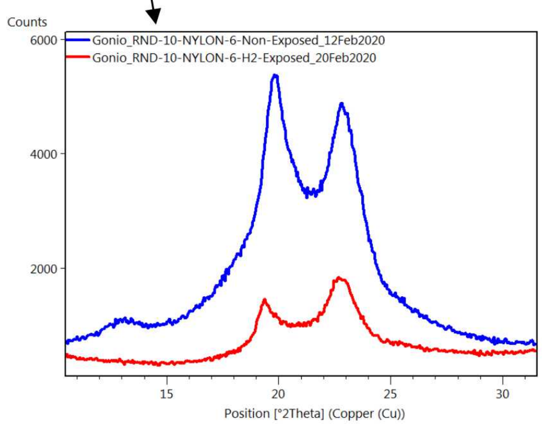
XRD of thermoplastics: 100 cycles of H_2

Nylon 66

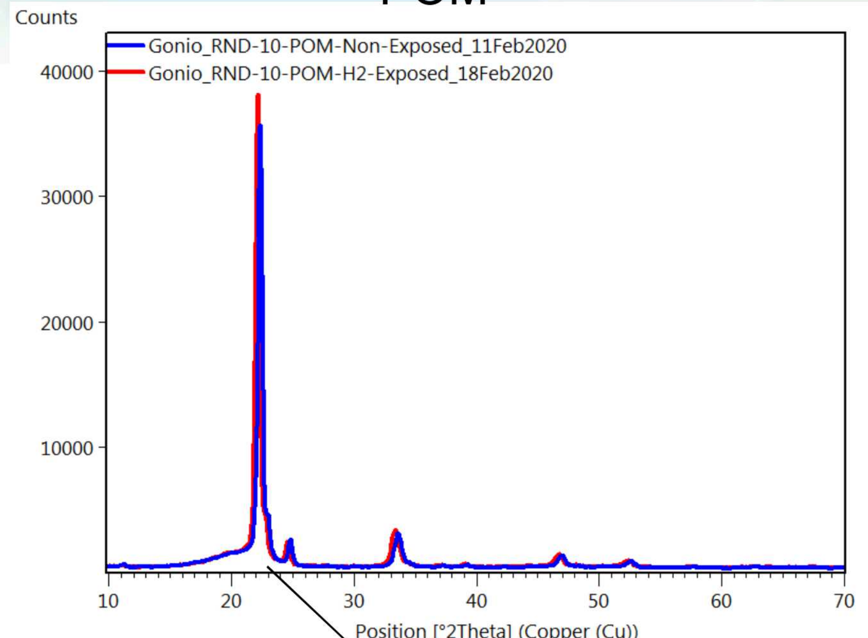


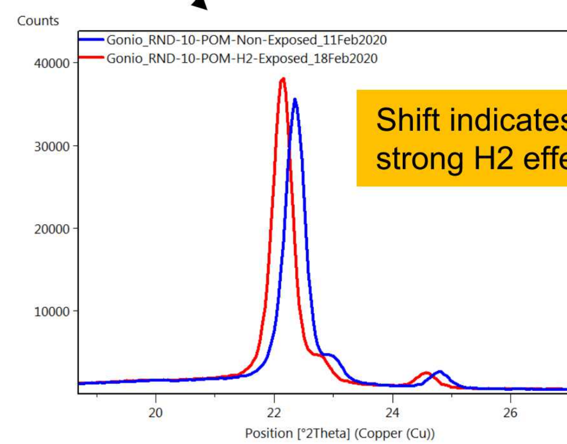


Not an artifact of the system

Reversal of peak intensities cannot be explained in Nylon 6,6: Real H2 effect ??

POM





Shift indicates a strong H2 effect

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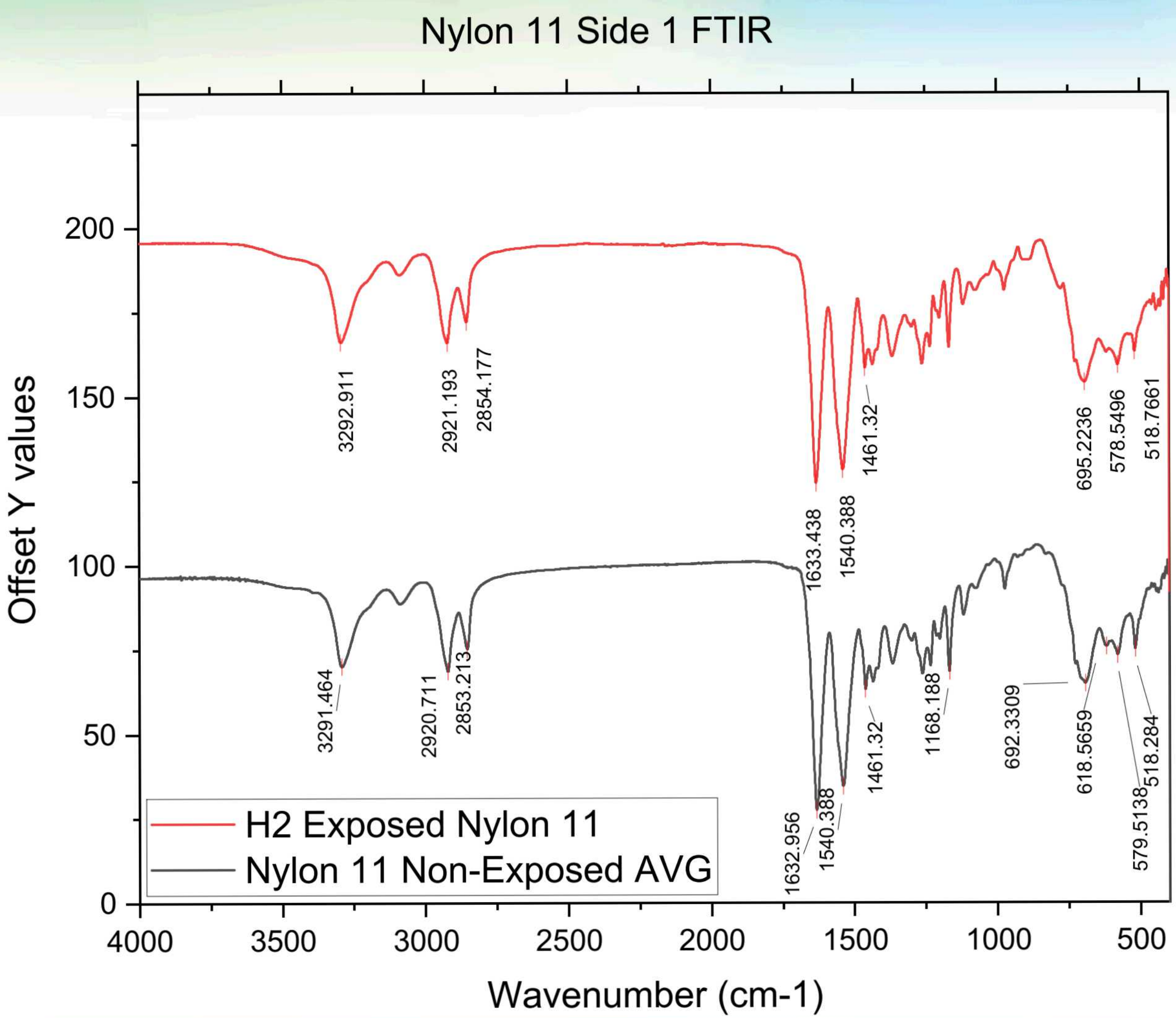
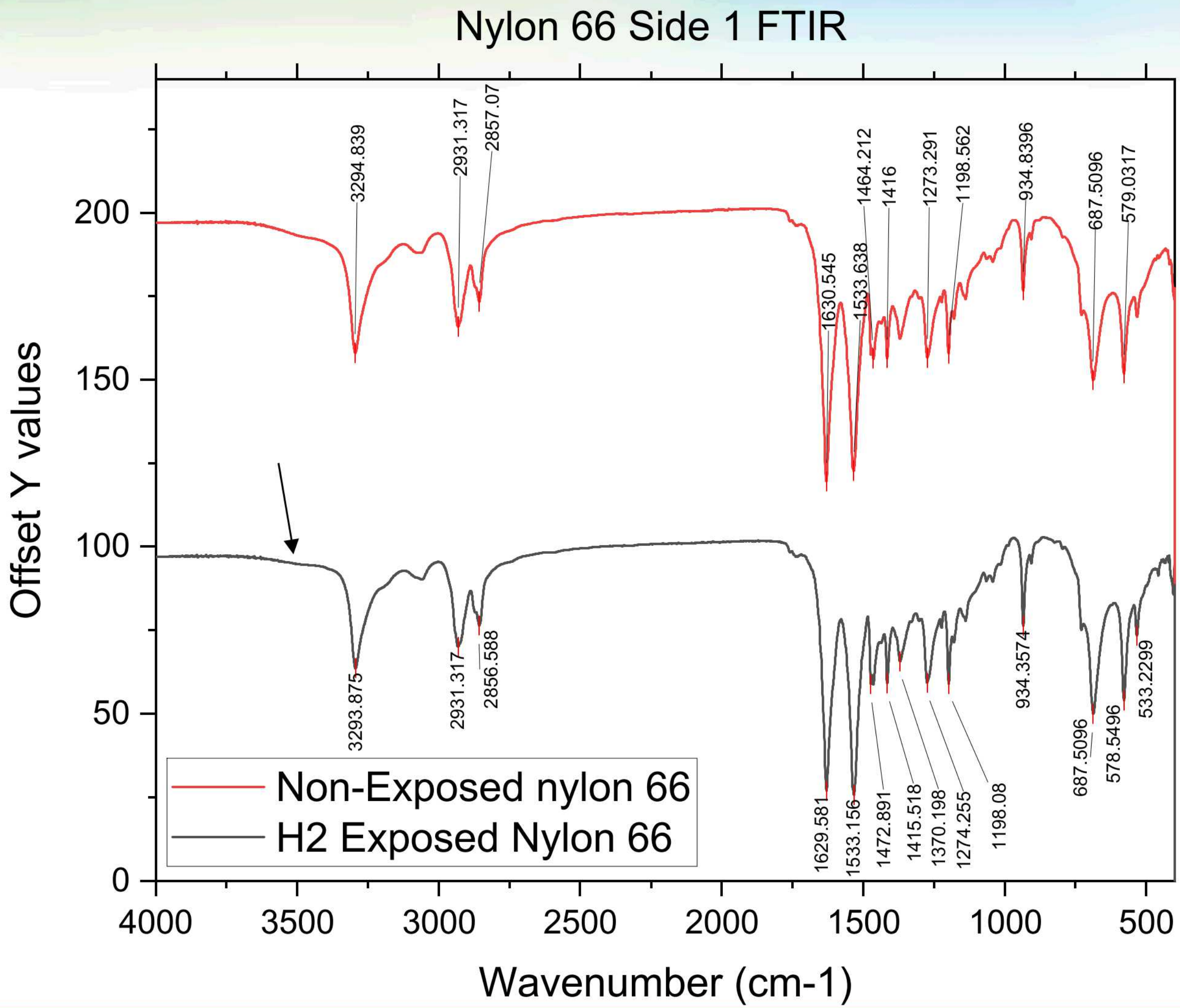
FT-IR of thermoplastics: 100 cycles of H_2



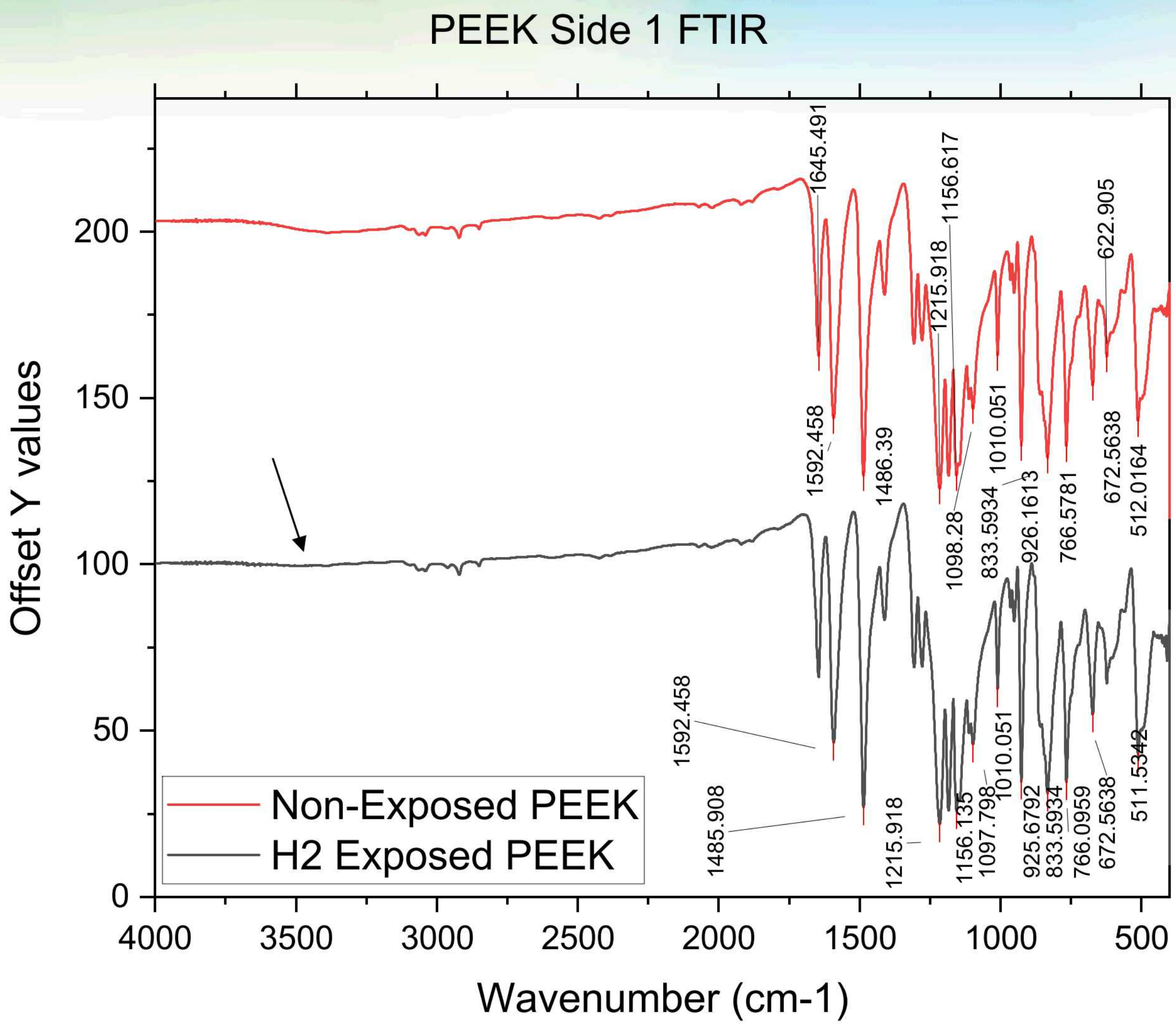
No chemical changes seen with Nylon 11 after H2 exposure

FT-IR of thermoplastics: 100 cycles of H_2



No chemical changes seen with Nylon 66 after H2 exposure

FT-IR of thermoplastics: 100 cycles of H_2



No chemical changes seen with PEEK after H2 exposure

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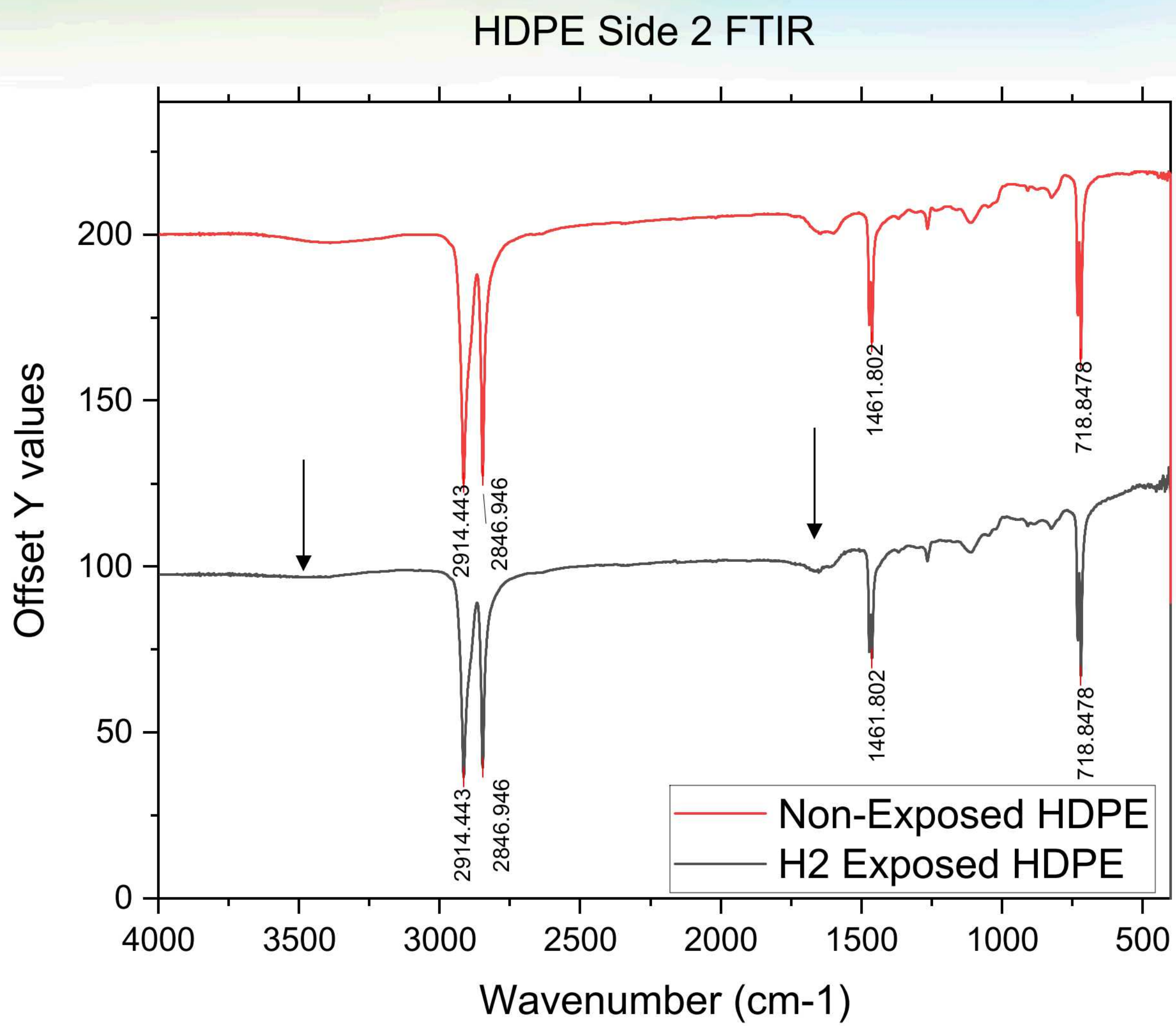
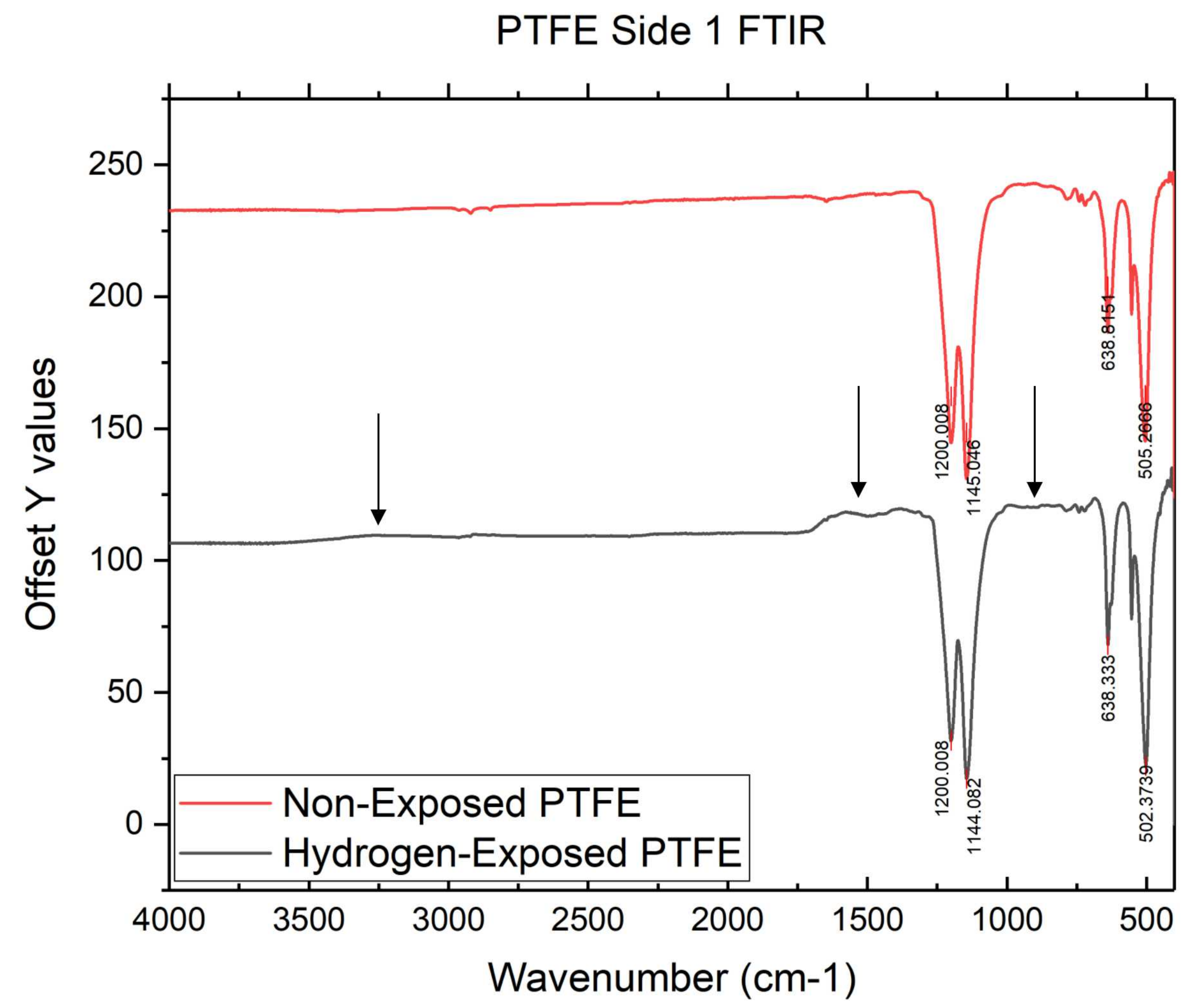
FT-IR of thermoplastics: 100 cycles of H_2



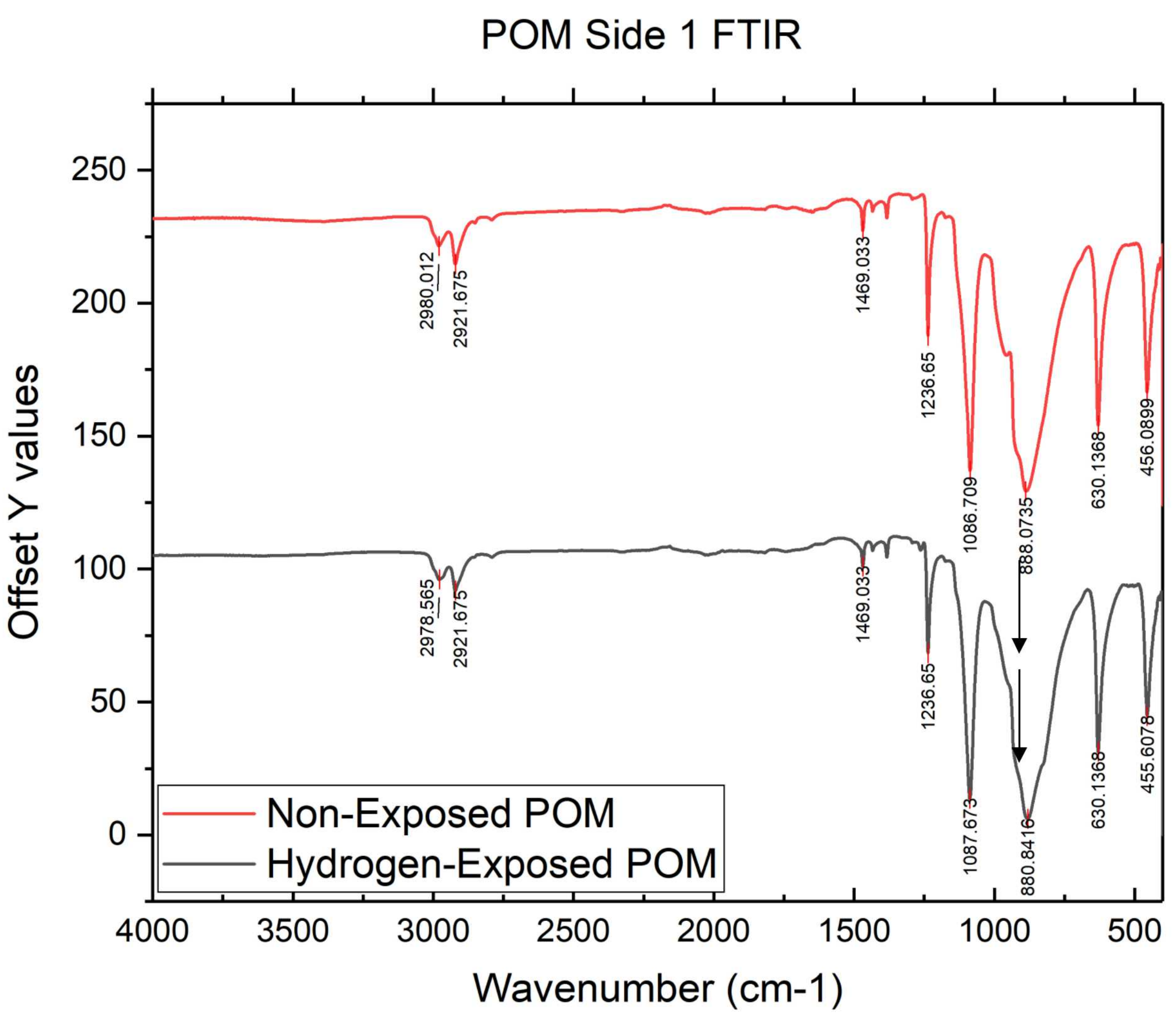
No significant chemical changes seen with HDPE after H2 exposure

FT-IR of thermoplastics: 100 cycles of H_2



No significant chemical changes seen with PTFE after H2 exposure

FT-IR of thermoplastics: 100 cycles of H_2



No significant chemical changes seen with HDPE after H2 exposure

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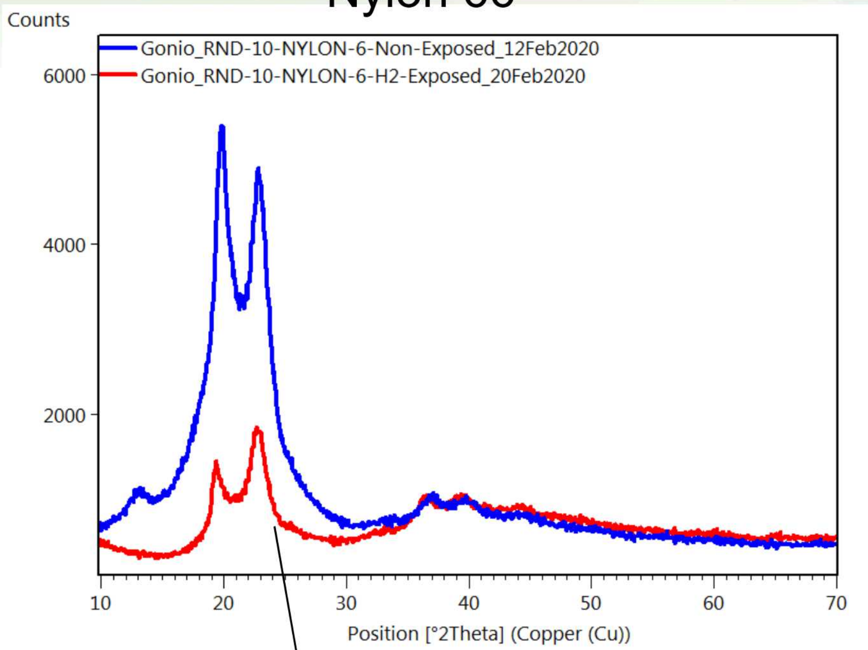
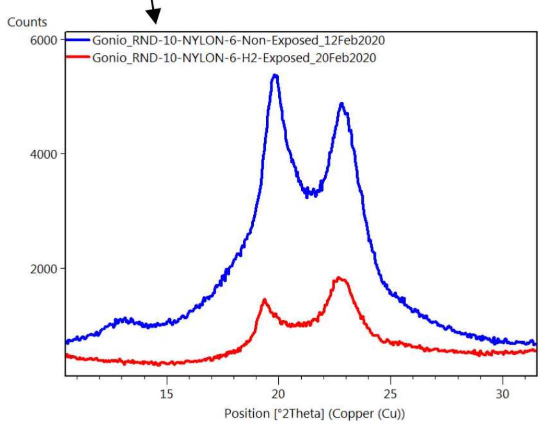
XRD of thermoplastics: 100 cycles of H_2

Nylon 66

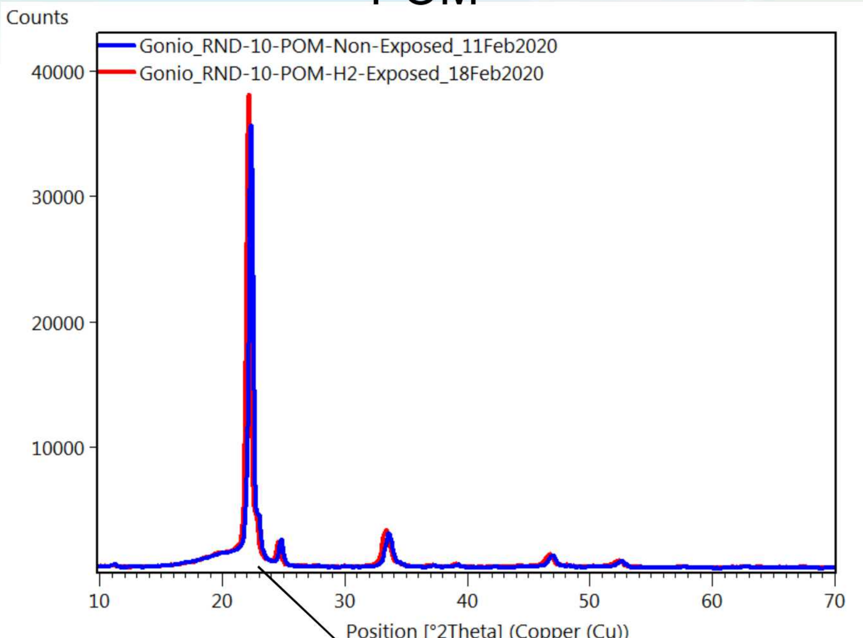


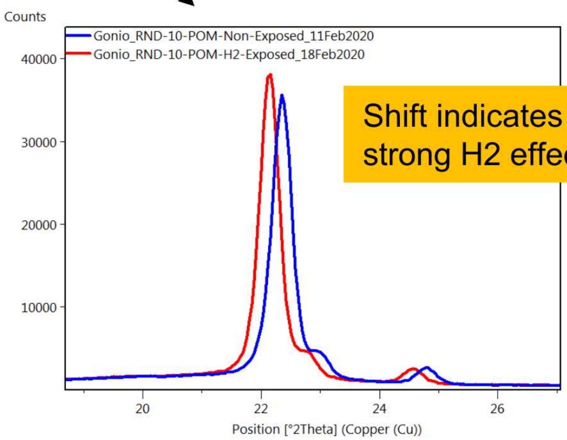


Not an artifact of the system

Reversal of peak intensities cannot be explained in Nylon 6,6: Real H2 effect ??

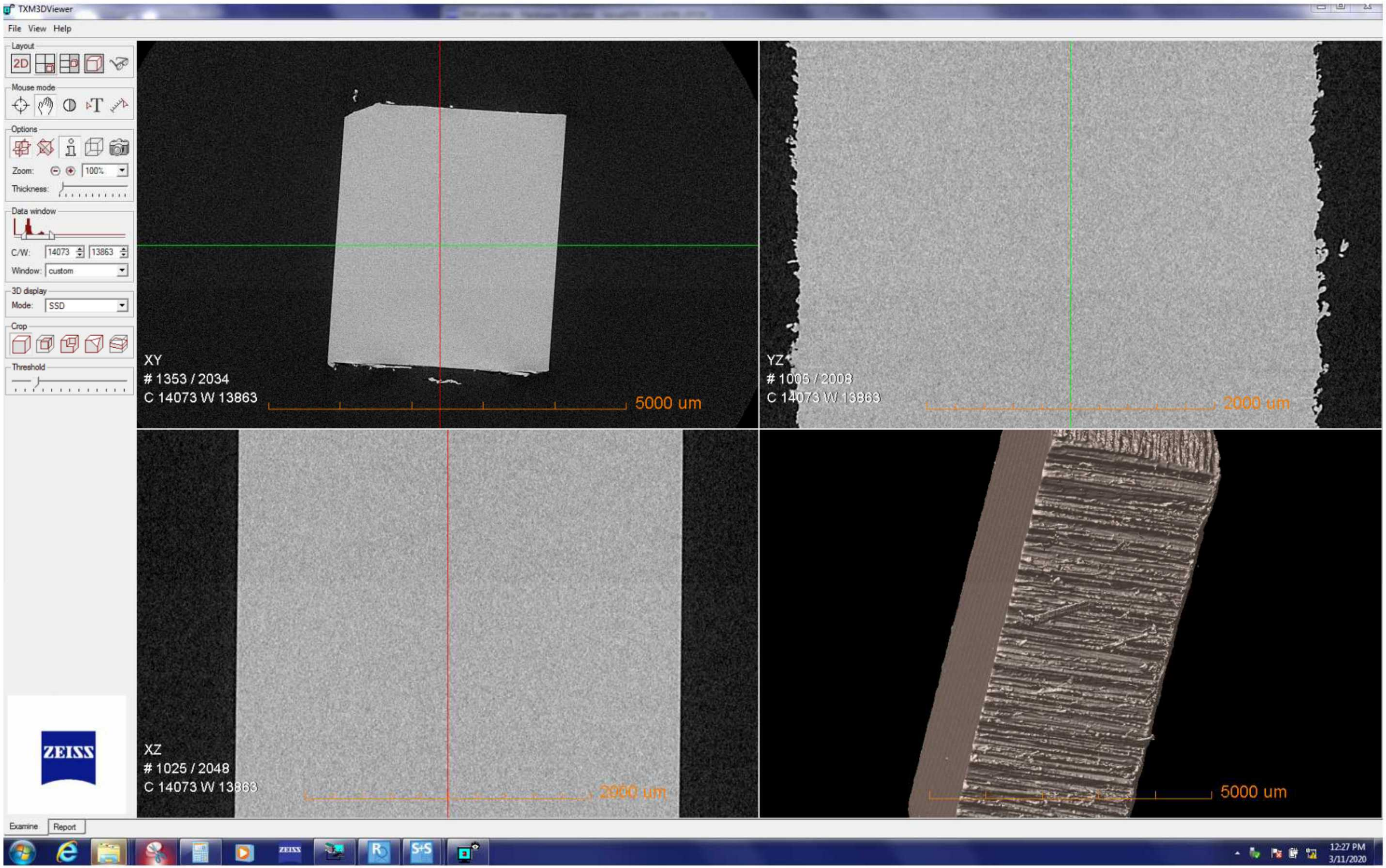
POM



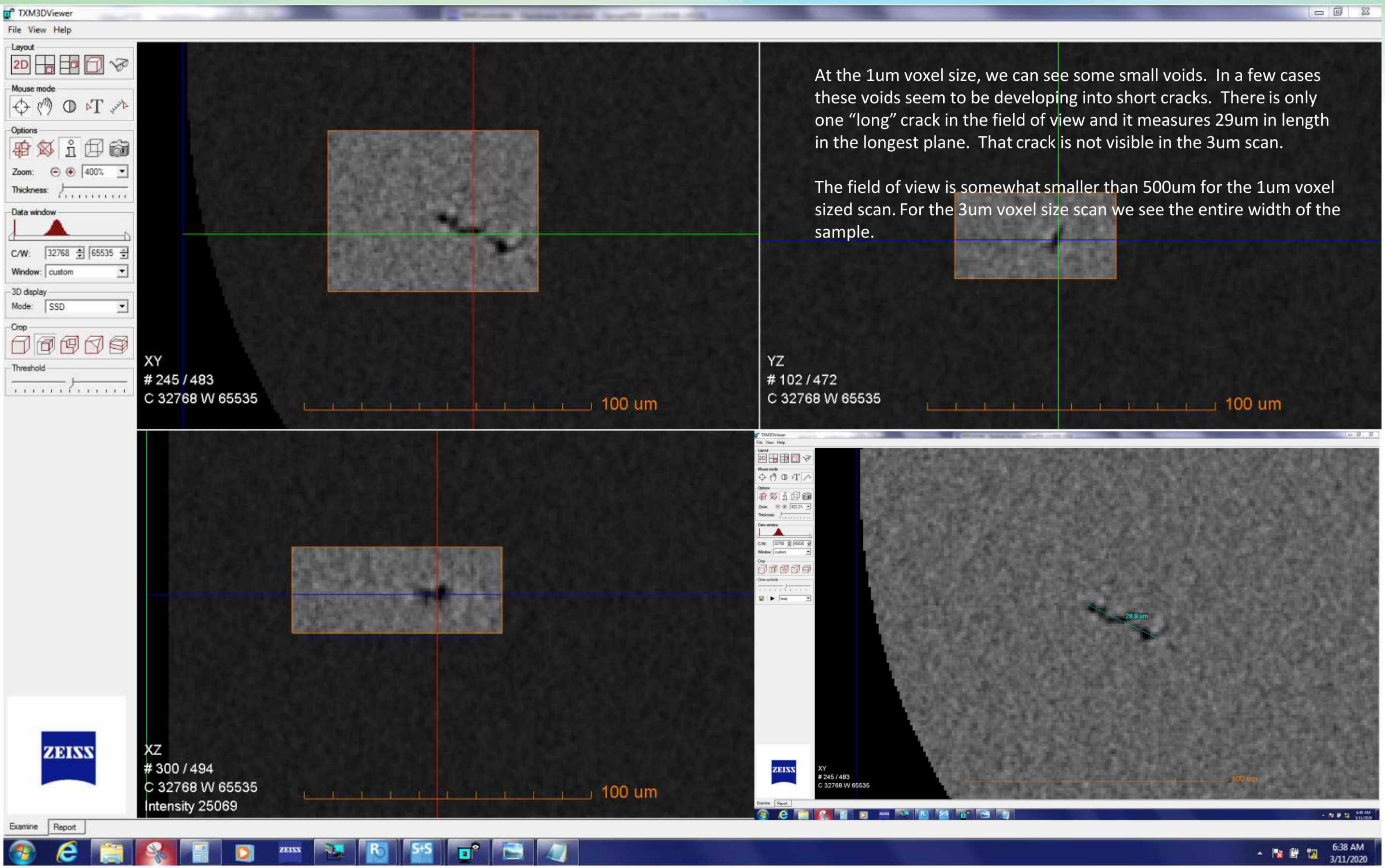


Shift indicates a strong H2 effect

Polyoxymethylene sample before exposure to H_2



Polyoxymethylene sample after exposure to H_2



At the 1um voxel size, we can see some small voids. In a few cases these voids seem to be developing into short cracks. There is only one “long” crack in the field of view and it measures 29um in length in the longest plane. That crack is not visible in the 3um scan.

The field of view is somewhat smaller than 500um for the 1um voxel sized scan. For the 3um voxel size scan we see the entire width of the sample.

Conclusions

- Elastomers and thermoplastics subjected to high pressure cycling H2 behave differently

- For elastomers, the highly cross-linked tight polymer network with limited free volume, and the presence of fillers and plasticizers play a significant role in providing H_2 resistance

- Plasticization of the matrix can be a possible mechanism for H_2 attack while filler-containing formulations show maximum change indicating interaction of carbon and silica with H_2

- The six thermoplastics tested (POM, PTFE, HDPE, PEEK, Nylon 6,6 and Nylon 11) for different physical, chemical and mechanical properties do not show substantial changes; however,
  - Onset of chemical changes was identified for H_2 cycled polymers
  - Chemical changes were seen best with Fourier Transform Infra Red Spectroscopy (FTIR), Solid state ^1H MAS NMR and X-ray Diffraction (XRD)

- Further cycling experiments for longer times, lower temperatures can reveal the influence of such physical stresses on mechanical properties of polymers in H2 service

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