SAND2024-16830C

Characterization Techniques (in-situ and ex-situ) for Polymers in H-MAT: **Raman and X-Ray Scattering**

Michael Leveille

12/17/24

2024 H-MAT Polymer Technical Exchange

Sandia National Laboratories, Livermore, CA

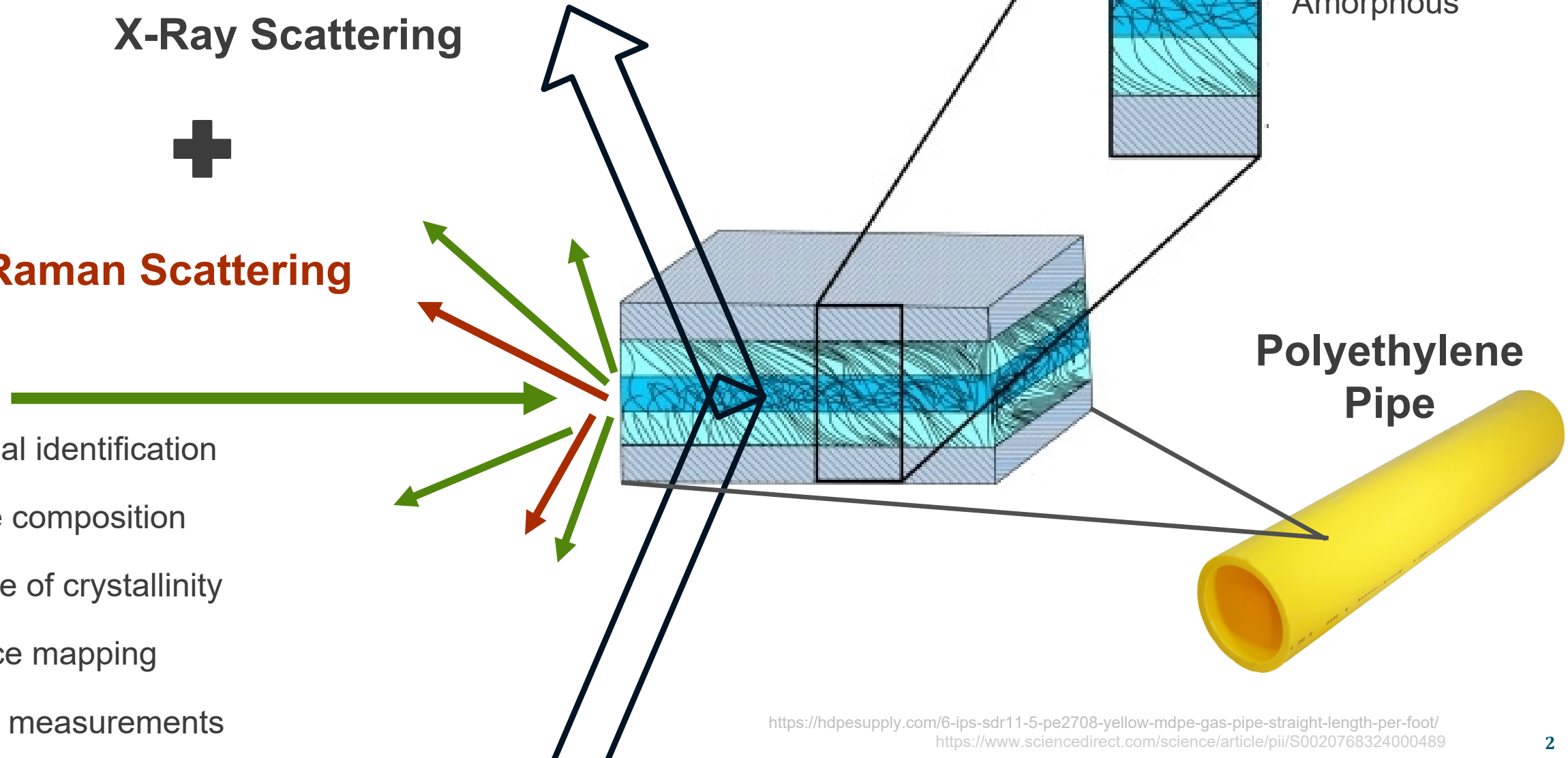
Sandia National Laboratories is a multimission laboratory managed and operated by National Technology & Engineering Solutions of Sandia, LLC, a wholly owned subsidiary of Honeywell International Inc., for the U.S. Department of Energy's National Nuclear Security Administration under contract DE-NA0003525.

Raman and X-ray Scattering

X-Ray Scattering

+

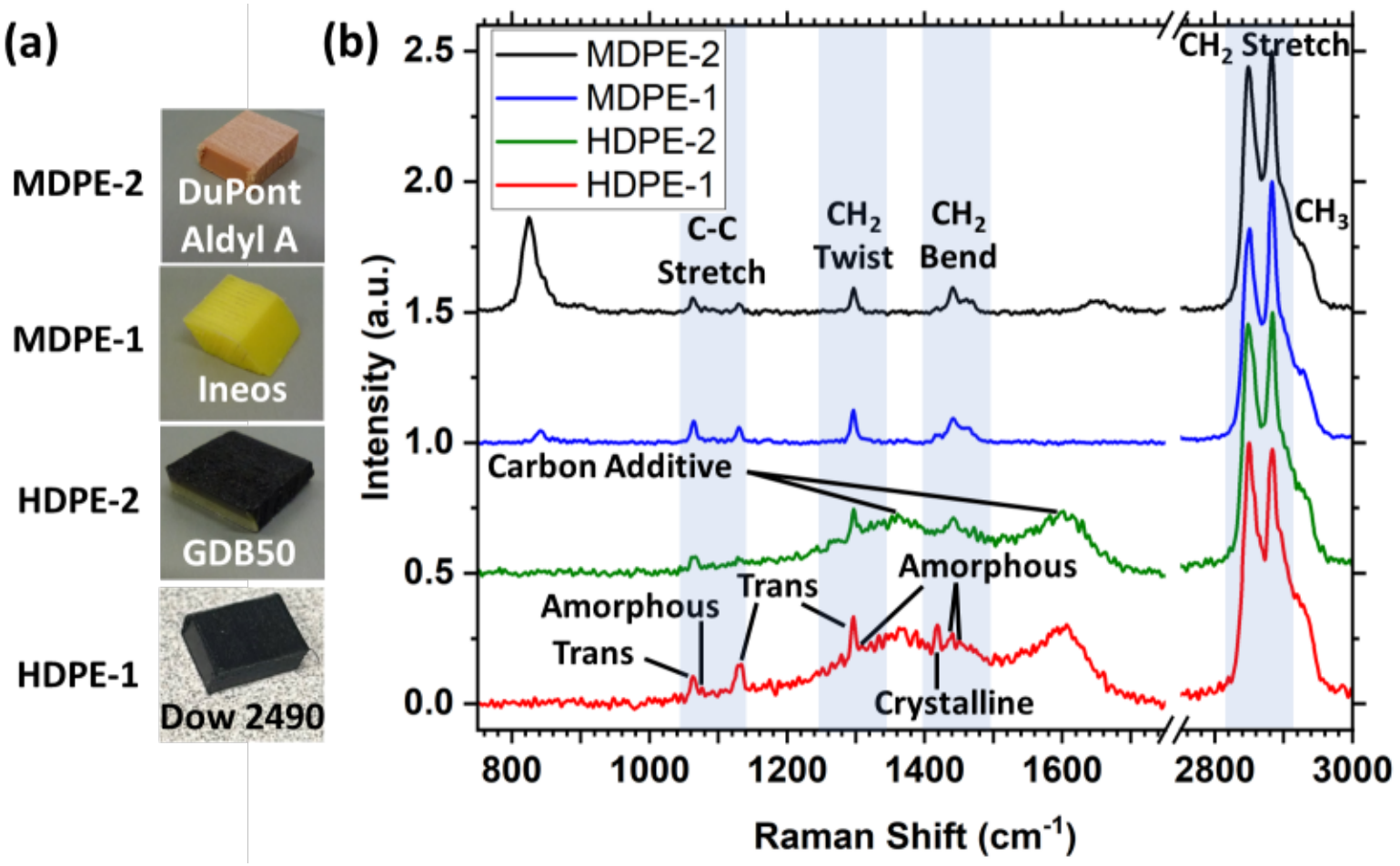
Raman Scattering

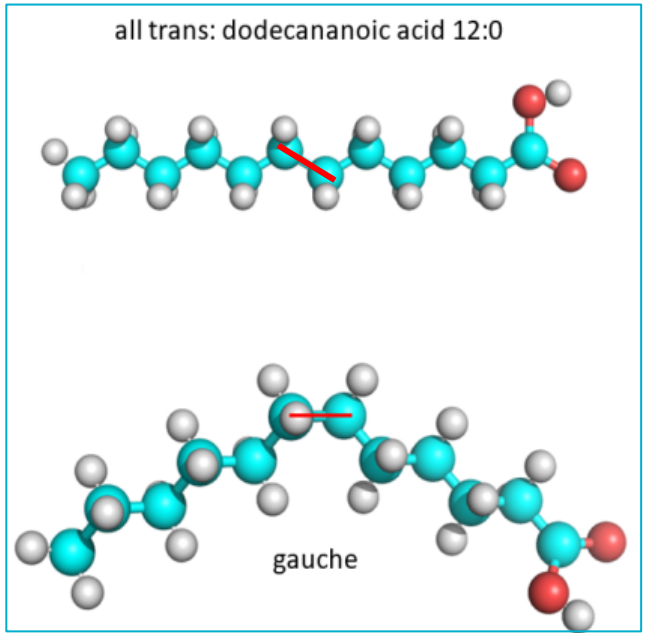


- Material identification
- Phase composition
- Degree of crystallinity
- Surface mapping
- In-situ measurements

https://hdpesupply.com/6-ips-sdr11-5-pe2708-yellow-mdpe-gas-pipe-straight-length-per-foot/
https://www.sciencedirect.com/science/article/pii/S0020768324000489

Raman Spectroscopy of Polyethylenes

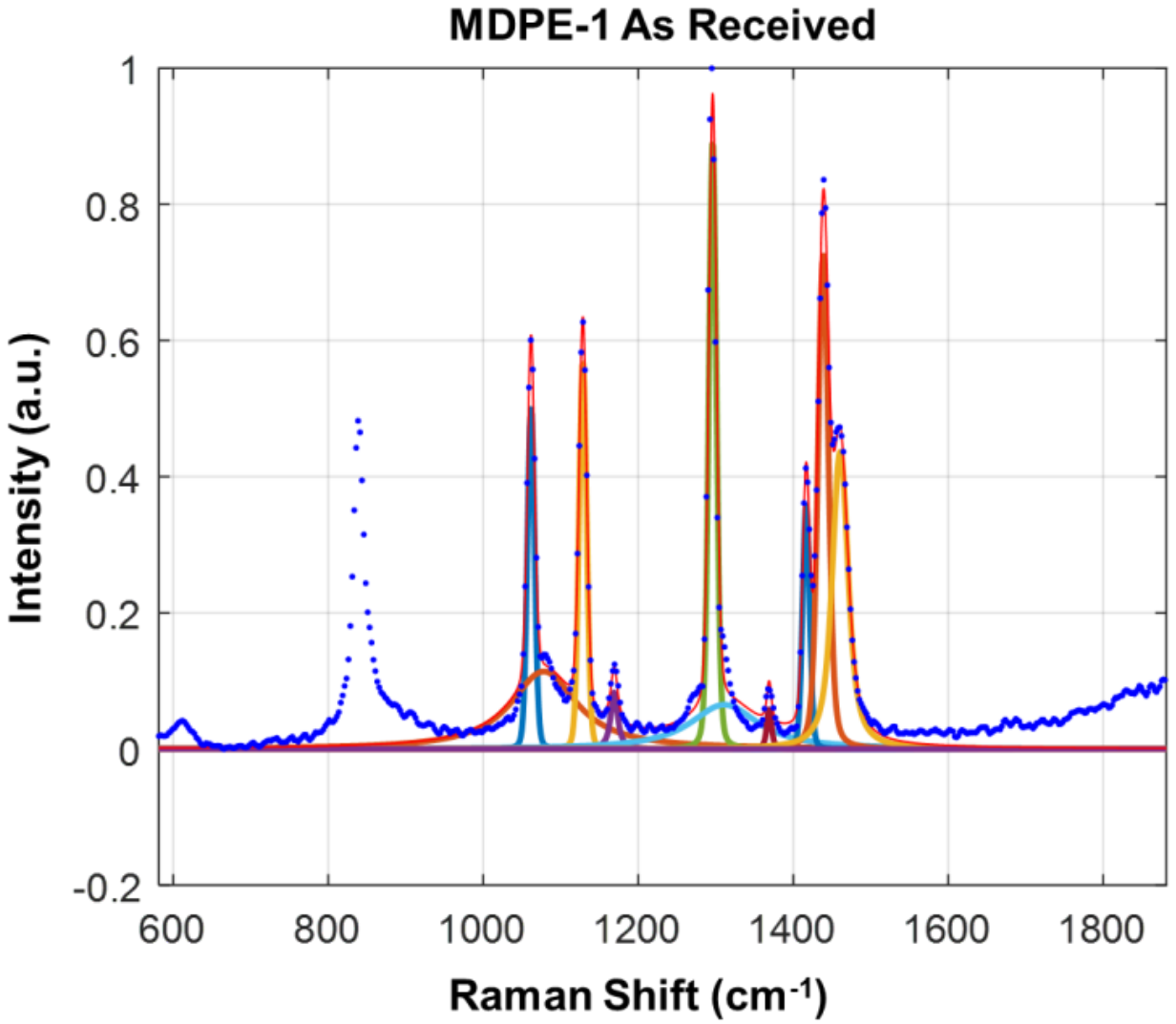




https://bio.libretexts.org/Bookshelves/Biochemistry/Fundamentals_of_Biochemistry_%28Jakubowski_and_Flatt%29/01%3A_Unit_I-_Structure_and_Catalysis/04%3A_The_Three-Dimensional_Structure_of_Proteins/4.01%3A_Main_Chain_Conformations

- Raman shift sensitive to molecular bond and chain conformation
- Trans chains found in crystalline and interphase regions
- Additives appear in spectra

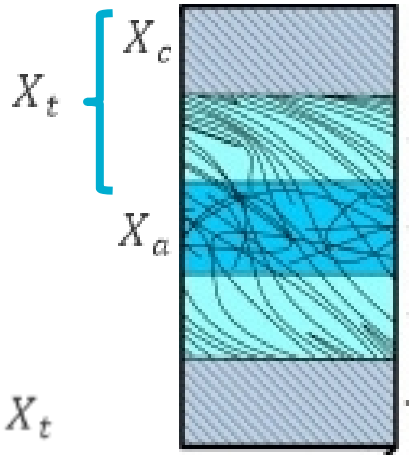
Raman Analysis – Peak Fitting and Intensity Ratios



$$X_c = \frac{I_{1418}}{A\left(I_{1298} + I_{1305}\right)}$$

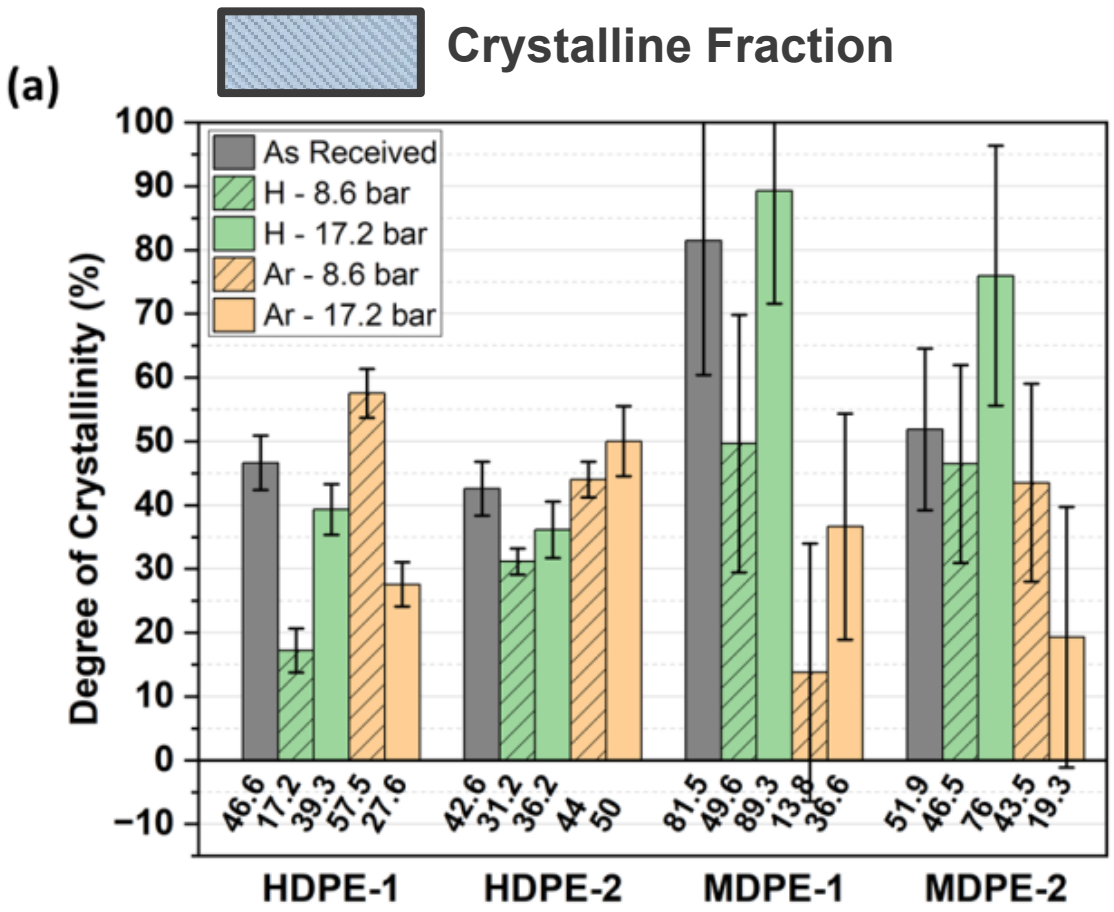
$$X_t = \frac{I_{1298}}{\left(I_{1298} + I_{1305}\right)}$$

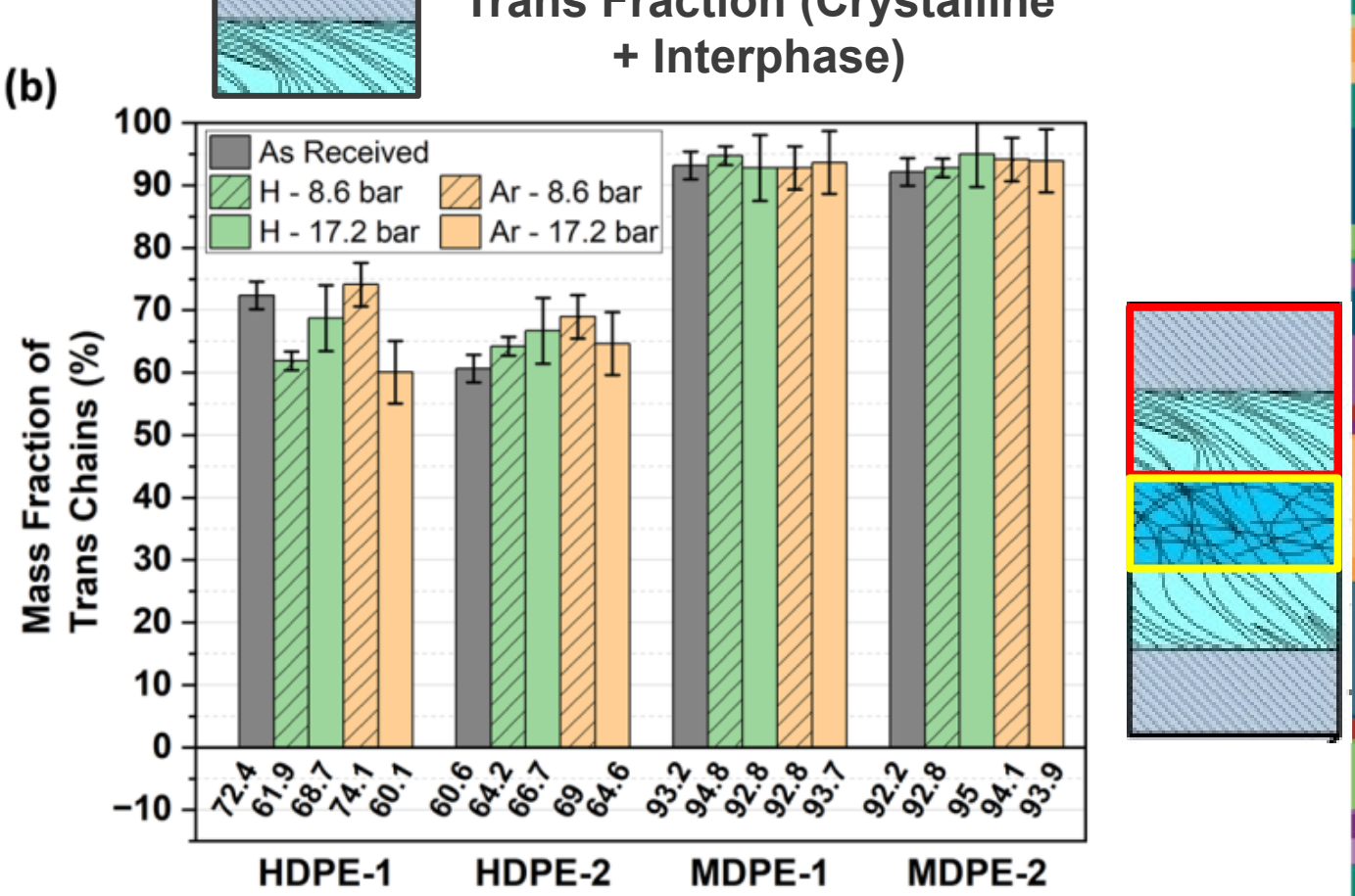
$$X_a = \frac{I_{1305}}{\left(I_{1298} + I_{1305}\right)} = 1 - X_t$$



Fitting Raman data allows us to calculate the mass fraction of crystalline, interphase, and amorphous regions

Raman Analysis – Phase Composition

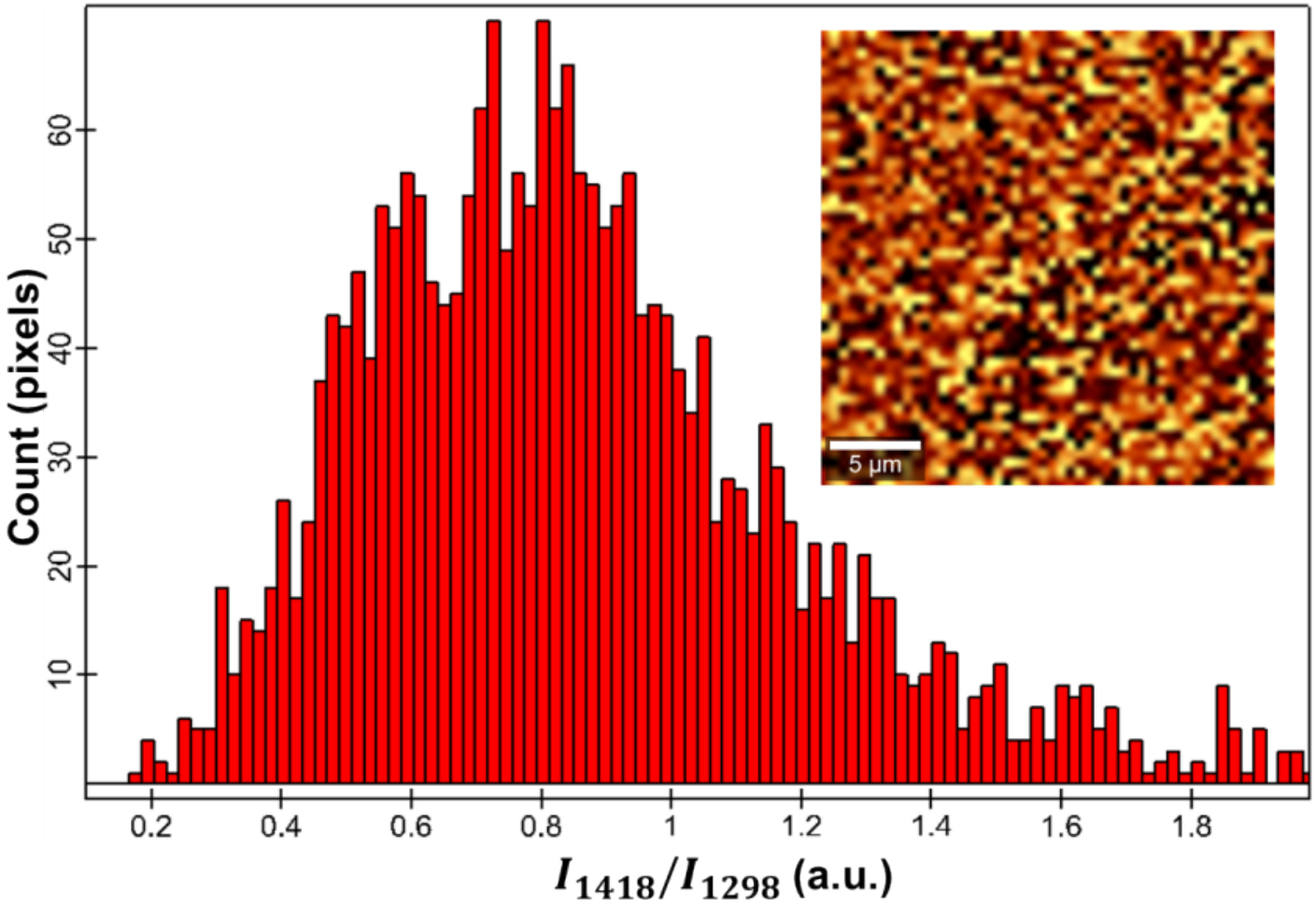


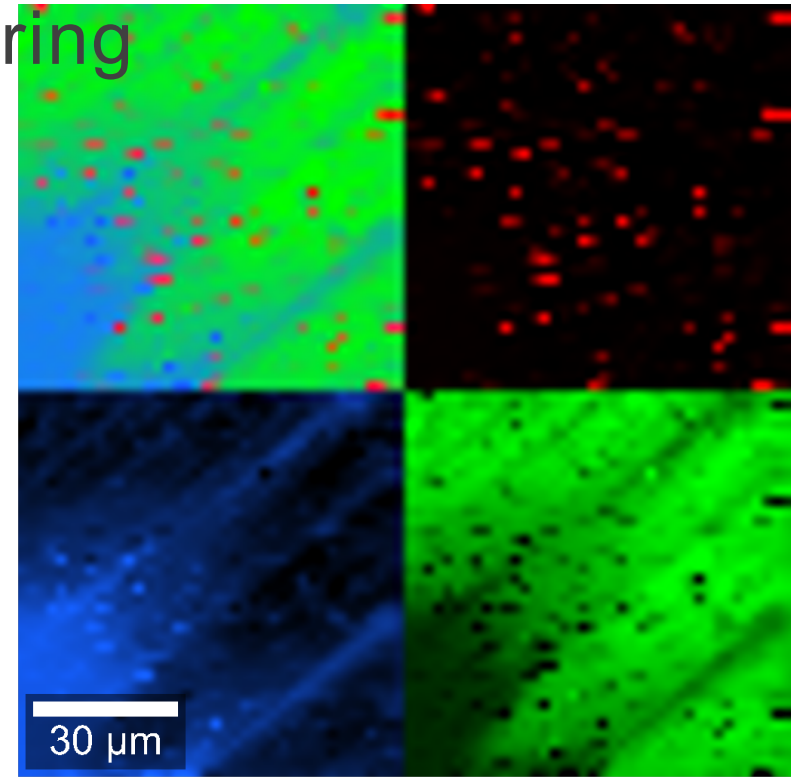


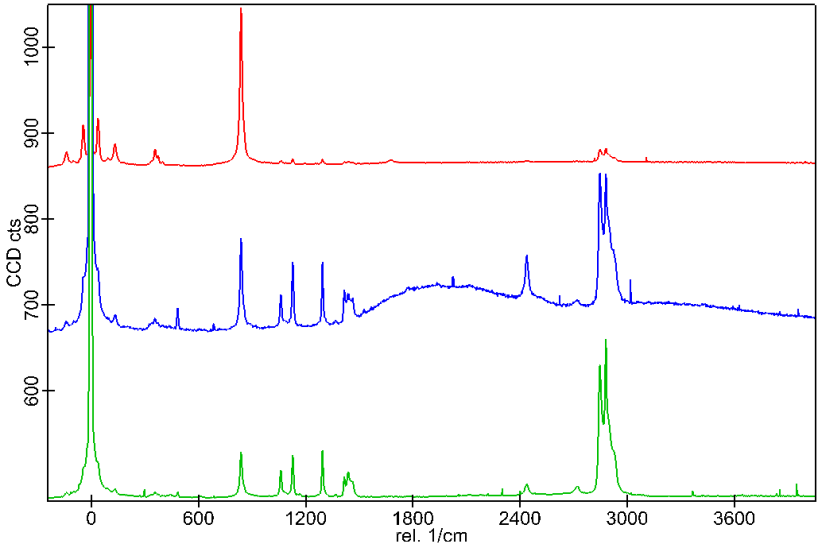
- Absolute DOC values inconsistent with DSC, need mapping to better characterize bulk
- No trend with gas exposure

Variation in crystallinity (exchange with interphase), potentially a surface property rather than gas effect, requiring surface mapping

Raman Analysis – Mapping and Clustering







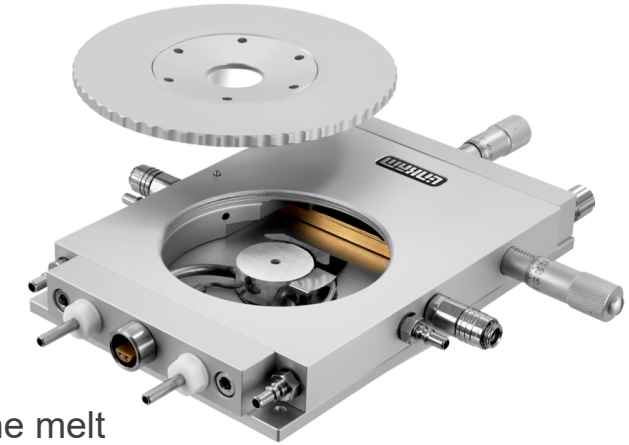
Raman mapping allows us capture surface variation, analyze homogenous regions and look for gas trends

In-situ Raman

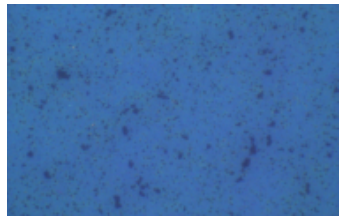
Linkam FTIR600 Stage

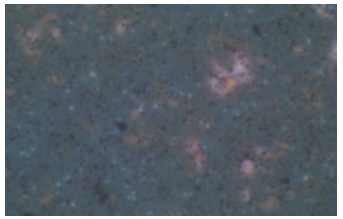
- Gas environment and temperature control with simultaneous imaging or Raman collections

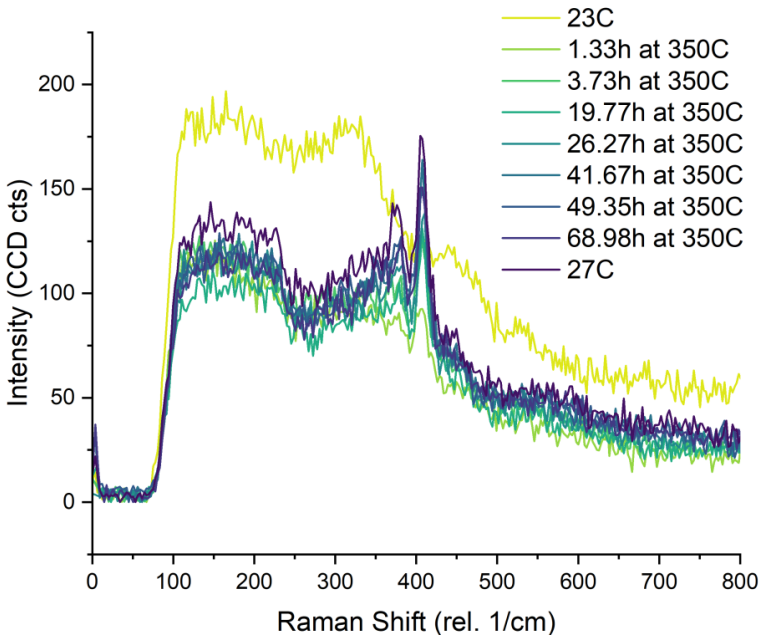
Linkam stage allows us to collect Raman data up to 600 C in different gas environments



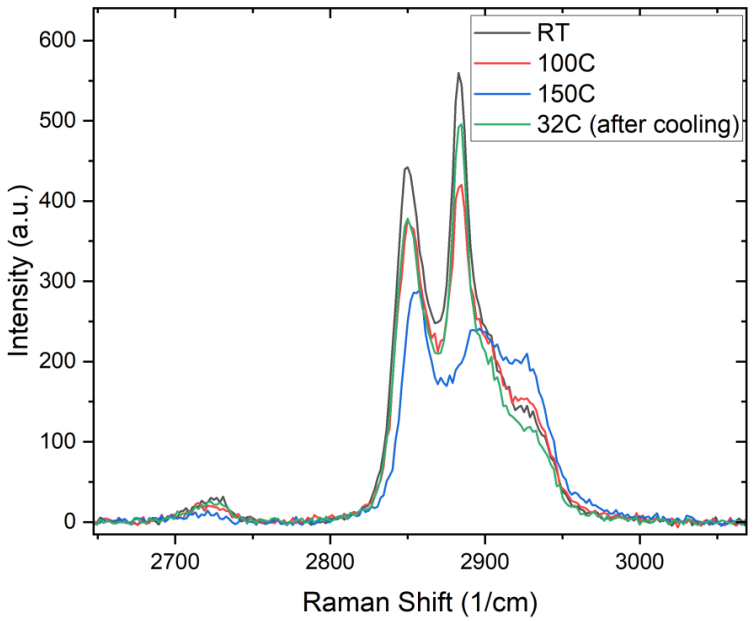
Ex. Raman spectra during MoS2 annealing in nitrogen

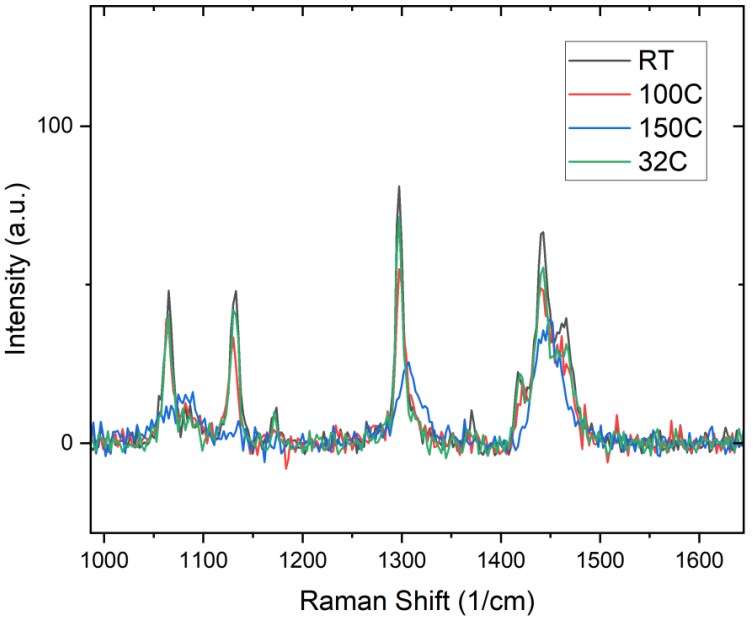






Ex. Comparing Raman spectrum of MDPE with the melt



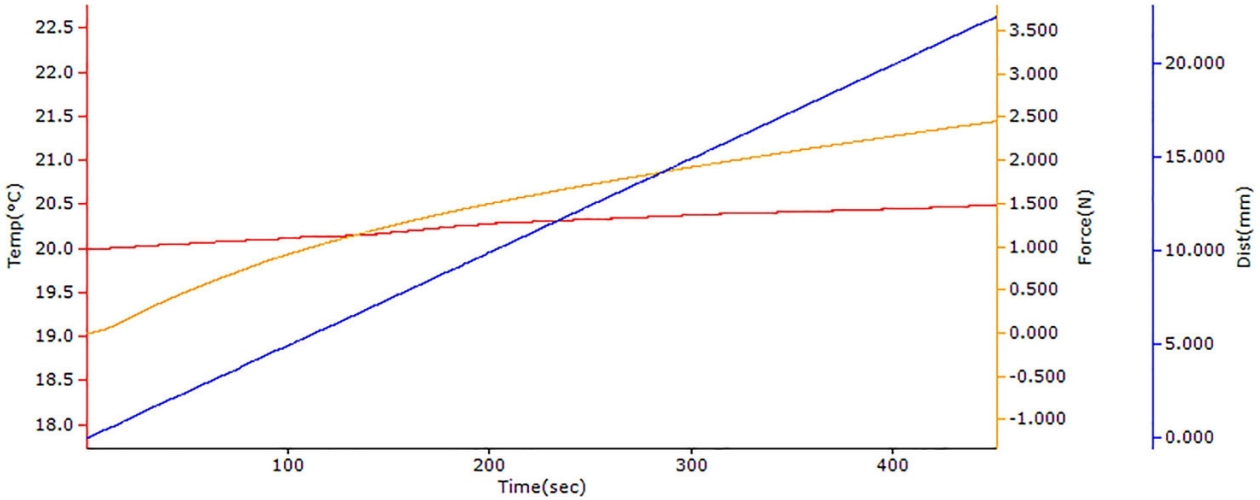


In-situ Raman

Modular Force Stage

- Tension, compression, multi-point bend
- Temp., humidity, gas environment

New stage allows us to simultaneously collect stress/strain curves and Raman data up to 600 C in different gas environments



Tensile Tests of MDPE Pipe After 250psi H_2 for 1 Month

Room Temperature

Comparable stiffness

Comparable peak stress

Variation in strain at onset of non-uniform deformation

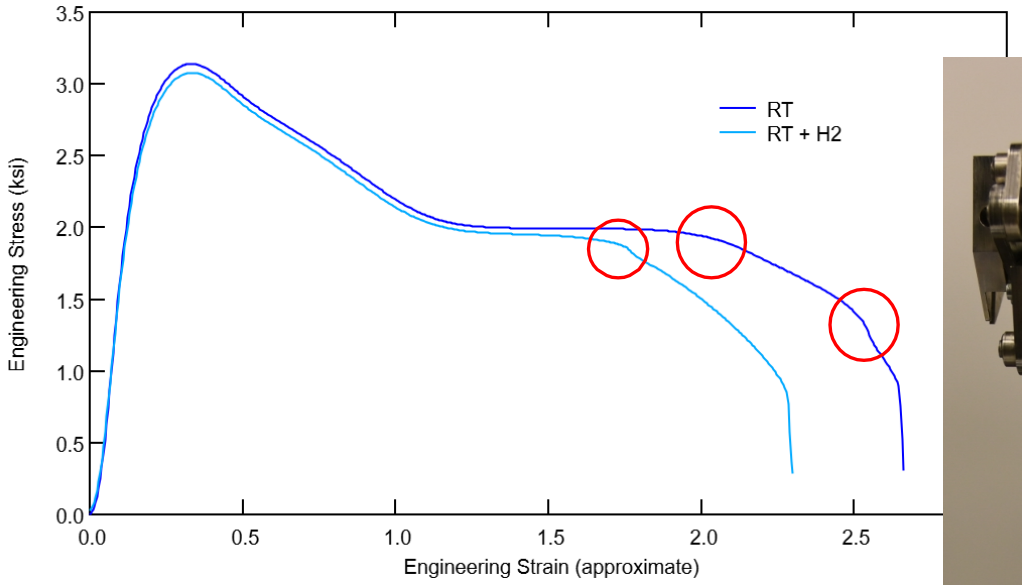
120 °C

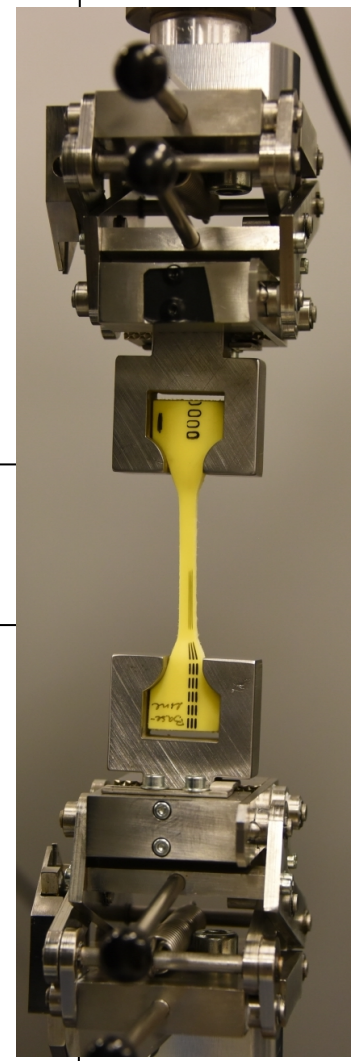
Comparable stiffness (both elastic and plastic)

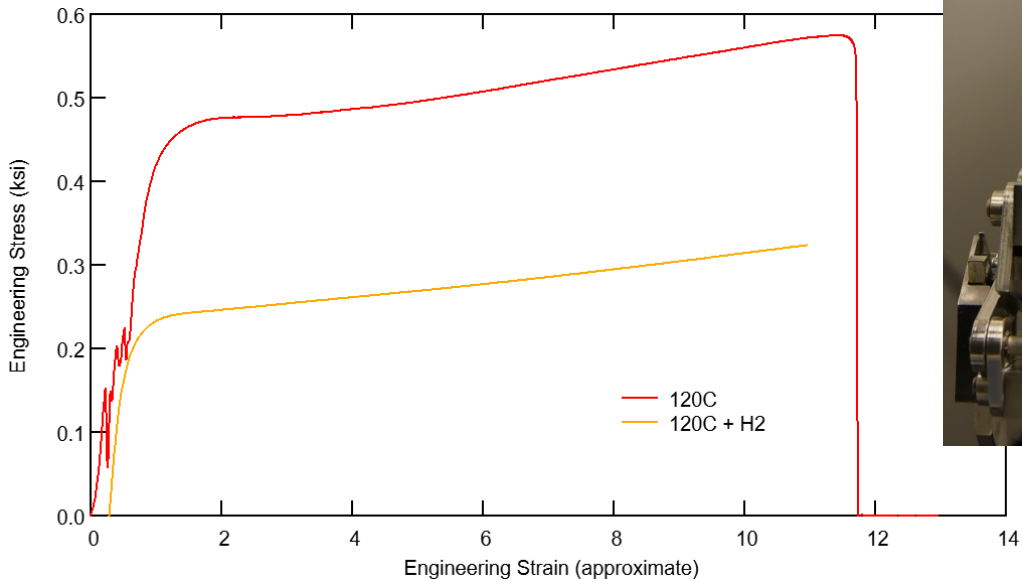
Stress is about halved in H_2 exposed specimen

*Time after decompression: 24h

Initial tests in study on the influence of strain rate and temperature on tensile performance of MDPE pipes exposed to hydrogen and hydrogen/methane gas blends



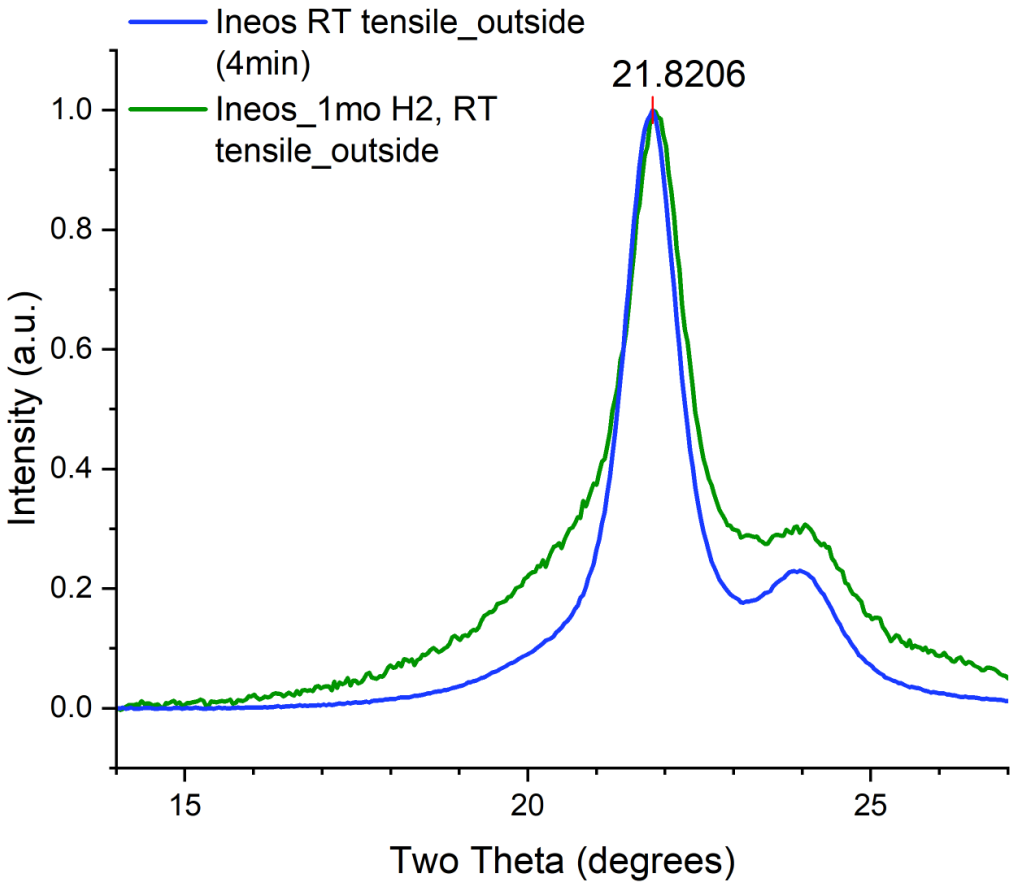


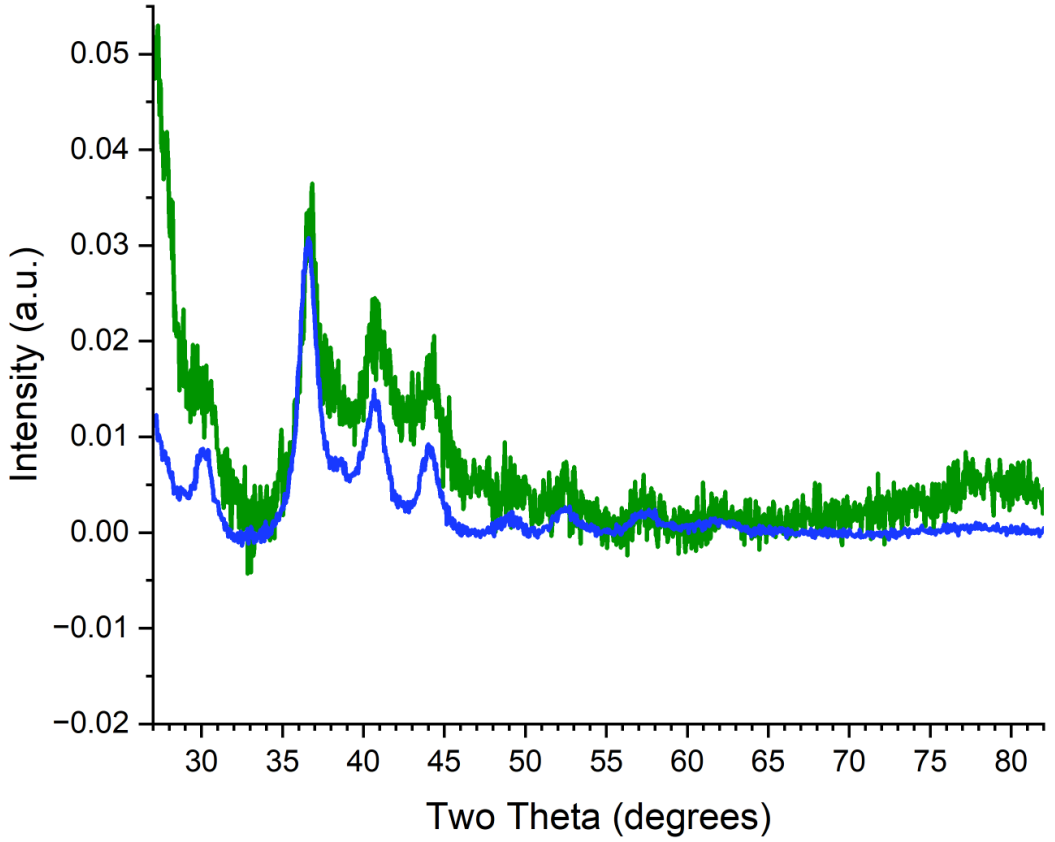


XRD of MDPE After Hydrogen Exposure and Tensile Testing

- Room temperature tensile tests
- As received vs 1mo 250psi H2

Hydrogen exposed samples appear less crystalline after RT tensile tests

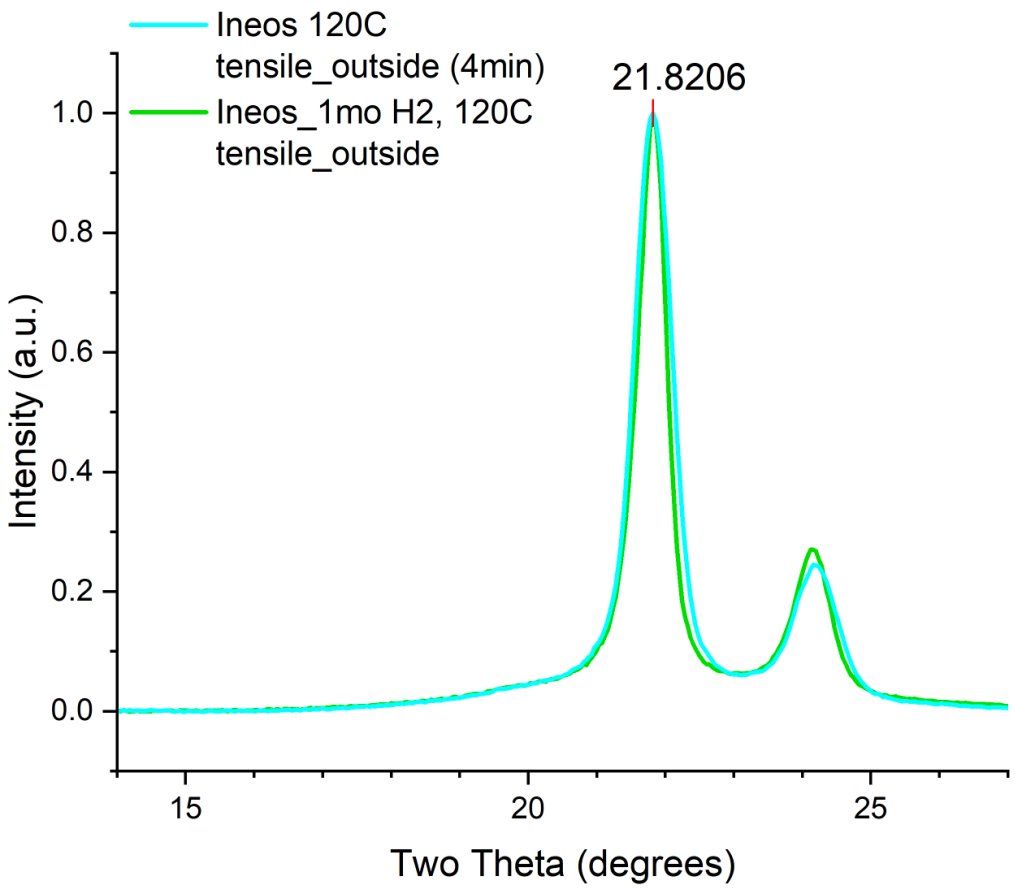


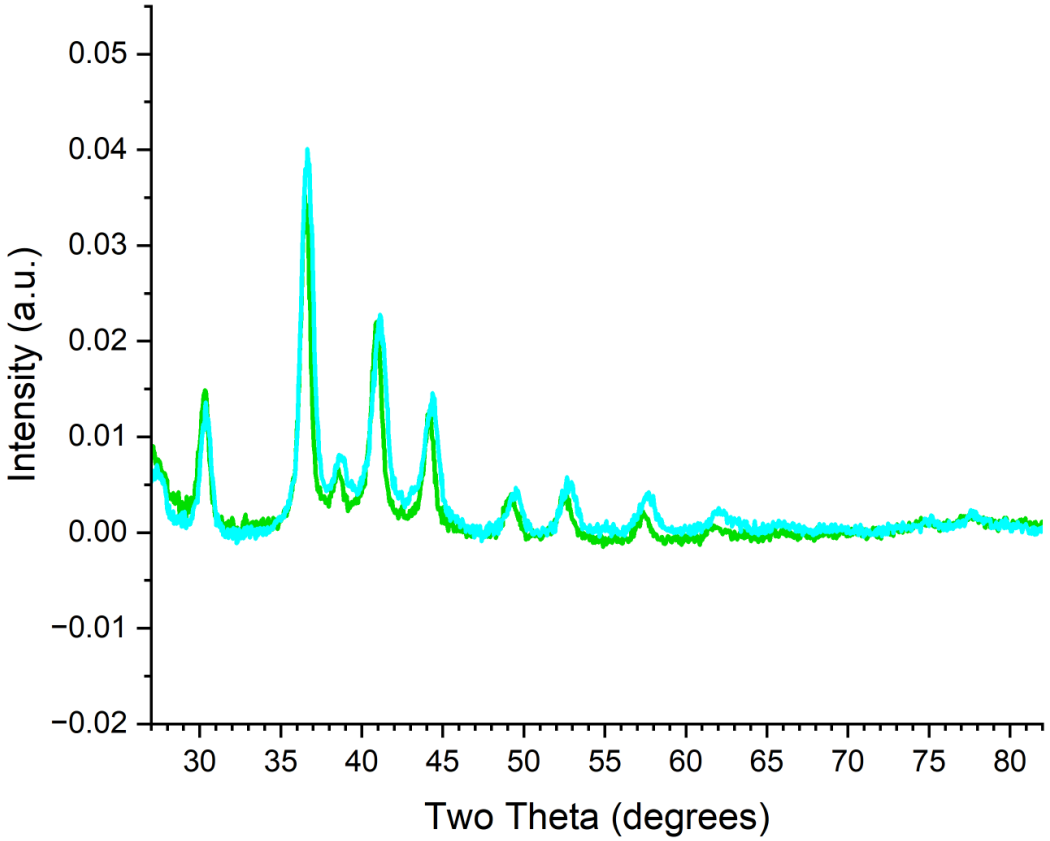


XRD of MDPE After Hydrogen Exposure and Tensile Testing

- Heated tensile tests
- As received vs 1mo 250psi H2

Hydrogen exposure has no affect on crystallinity after high temp. tensile tests

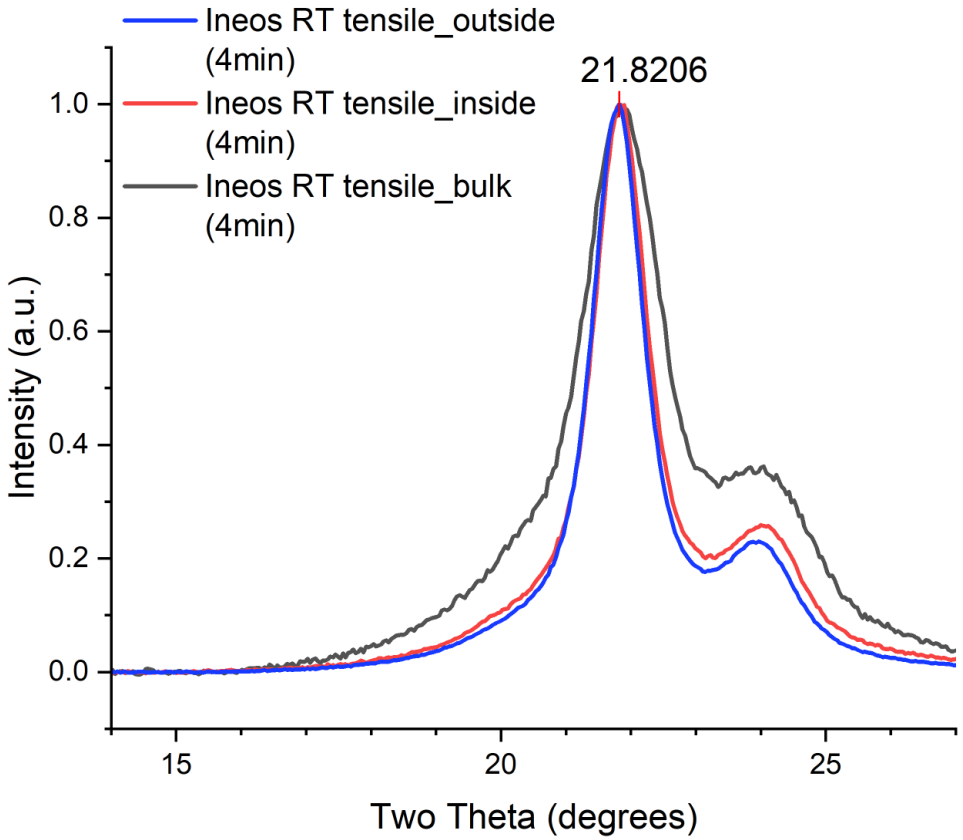




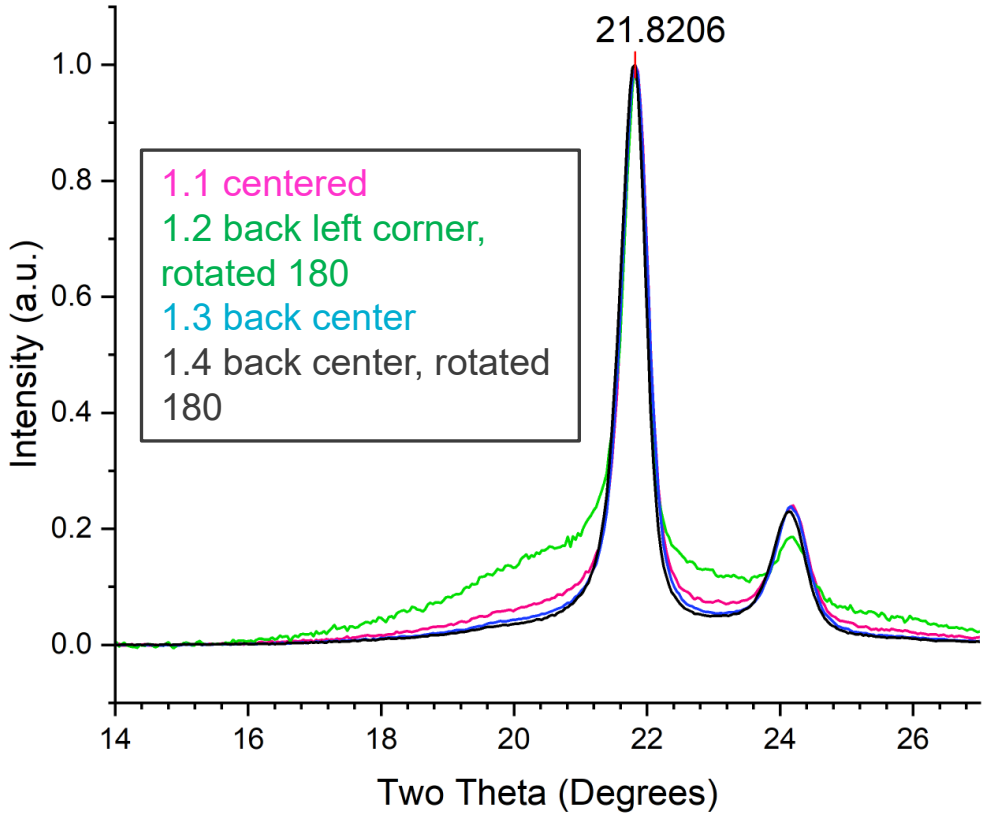
XRD – Challenges

- Small adjustments of sample placement/shape affect the peak ratios and intensity
- Non-standard sample shape after tensile tests
- 3D printed nylon stage contributes to the amorphous counts
- XRD pattern (degree of crystallinity and peak ratios) dependent on pipe location

Sensitivity to Pipe Location



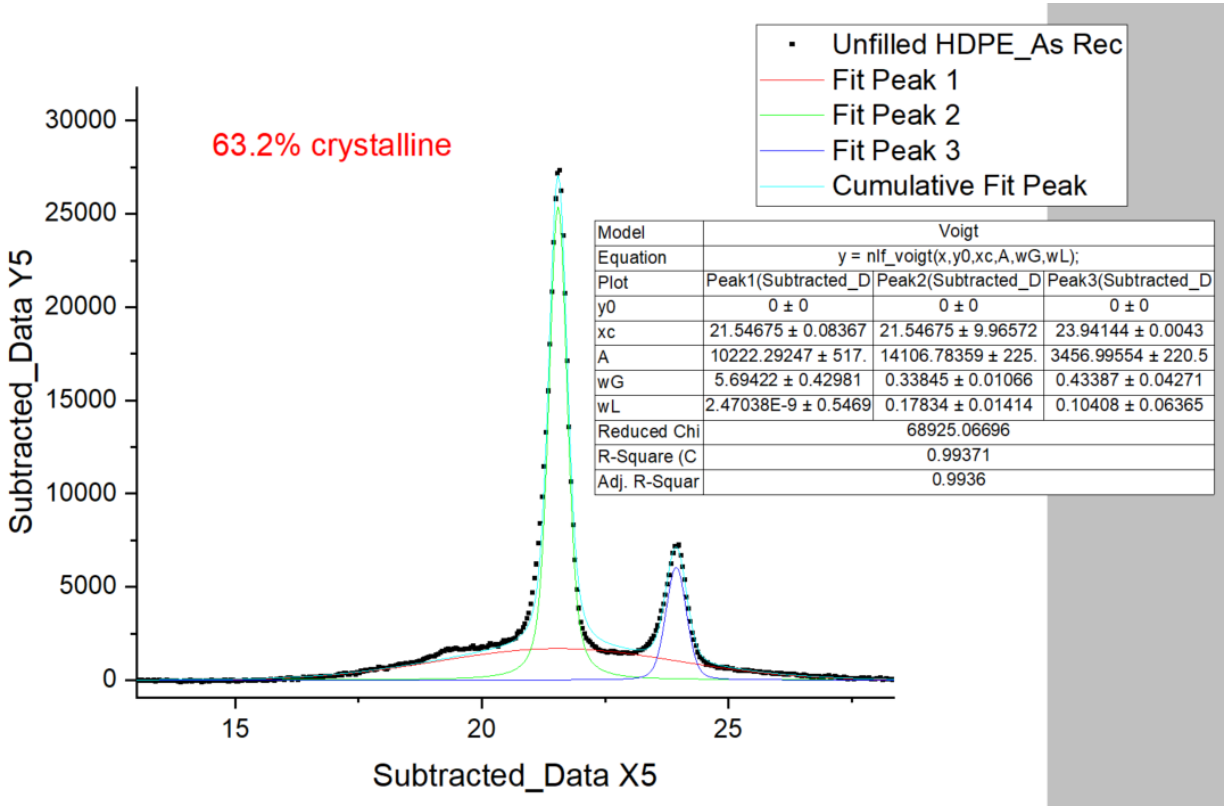
Sensitivity to Sample Placement



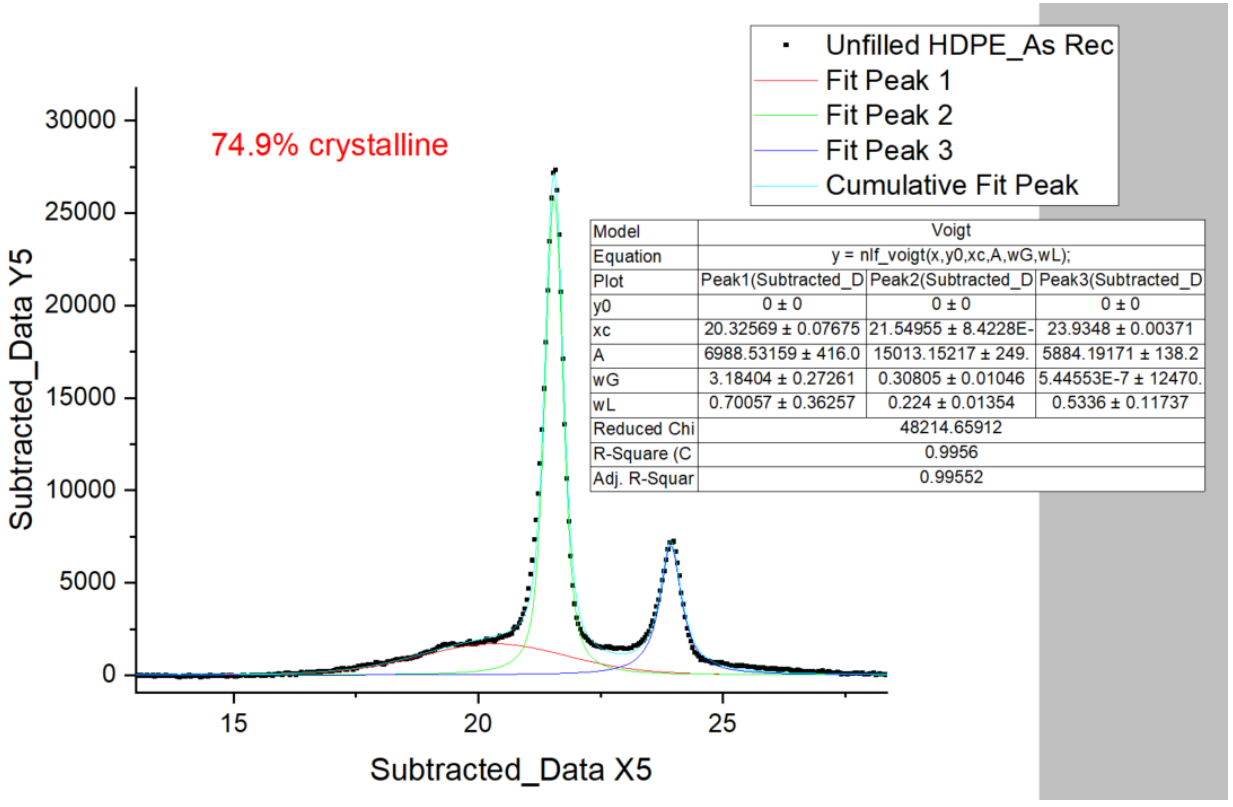
XRD – Challenges

Crystallinity very sensitive to fit

- How to choose parameters and fit properly?
- How to remove amorphous contribution from nylon stage?



Model	Voigt		
Equation	y = nlf_voigt(x,y0,xc,A,wG,wL);		
Plot	Peak1(Subtracted_D	Peak2(Subtracted_D	Peak3(Subtracted_D
y0	0 ± 0	0 ± 0	0 ± 0
xc	21.54675 ± 0.08367	21.54675 ± 9.96572	23.94144 ± 0.0043
A	10222.29247 ± 517.	14106.78359 ± 225.	3456.99554 ± 220.5
wG	5.69422 ± 0.42981	0.33845 ± 0.01066	0.43387 ± 0.04271
wL	2.47038E-9 ± 0.5469	0.17834 ± 0.01414	0.10408 ± 0.06365
Reduced Chi	68925.06696		
R-Square (C	0.99371		
Adj. R-Squar	0.9936		



Model	Voigt		
Equation	y = nlf_voigt(x,y0,xc,A,wG,wL);		
Plot	Peak1(Subtracted_D	Peak2(Subtracted_D	Peak3(Subtracted_D
y0	0 ± 0	0 ± 0	0 ± 0
xc	20.32569 ± 0.07675	21.54955 ± 8.4228E-	23.9348 ± 0.00371
A	6988.53159 ± 416.0	15013.15217 ± 249.	5884.19171 ± 138.2
wG	3.18404 ± 0.27261	0.30805 ± 0.01046	5.44553E-7 ± 12470.
wL	0.70057 ± 0.36257	0.224 ± 0.01354	0.5336 ± 0.11737
Reduced Chi	48214.65912		
R-Square (C	0.9956		
Adj. R-Squar	0.99552		

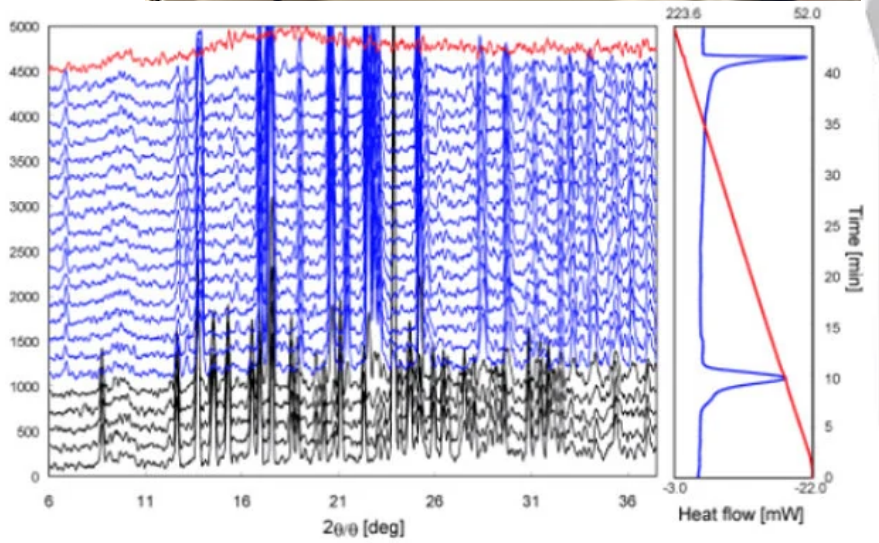
In-Situ XRD

In-situ Hydrogen

- Panalytical Empyrean w/ XRK 900 chamber
- 10 bar pressure plus temperature control

In-situ temp. and humidity w/ DSC

- Rigaku Smartlab
- Simultaneous DSC-XRD



THANK YOU