Pacific Northwest NATIONAL LABORATORY

Proudly Operated by Battelle *Since 1965*

Polymer / Elastomer and Composite Material Science

KEVIN L. SIMMONS

Pacific Northwest National Laboratory, Richland, WA

DOE Headquarters, Forrestal Bldg.
October 17-18, 2012

Outline

- Hydrogen production, transmission, distribution, delivery system
- Common themes in the hydrogen system
- Automotive vs infrastructure
- Hydrogen use conditions
- Polymer/elastomer and composites compatibility?
- Common materials in BOP components, hoses, and liners
- Common materials in composite tank and piping
- Material issues
  - Polymers/Elastomers
  - Composites
- Questions

Main Points to Remember

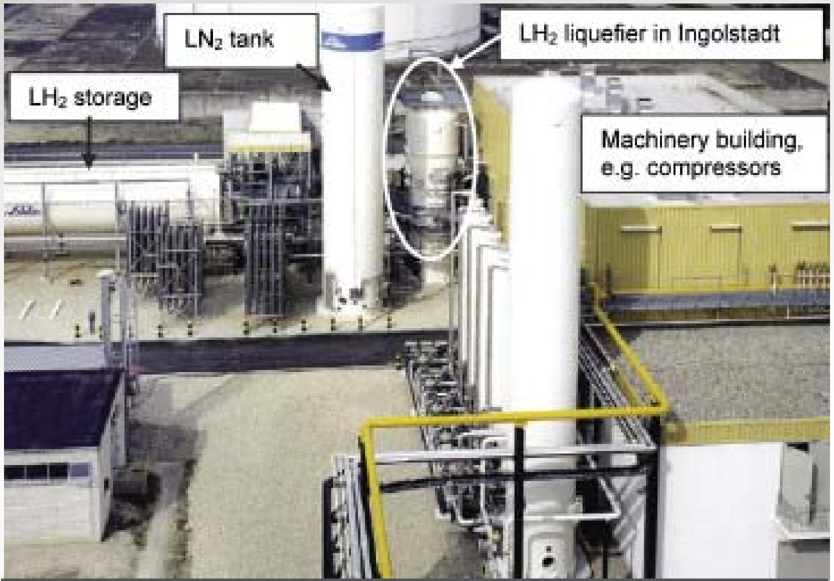
1) Polymers are extensively used in hydrogen and fuel cell applications

2) Hydrogen impact on polymers is not well understood

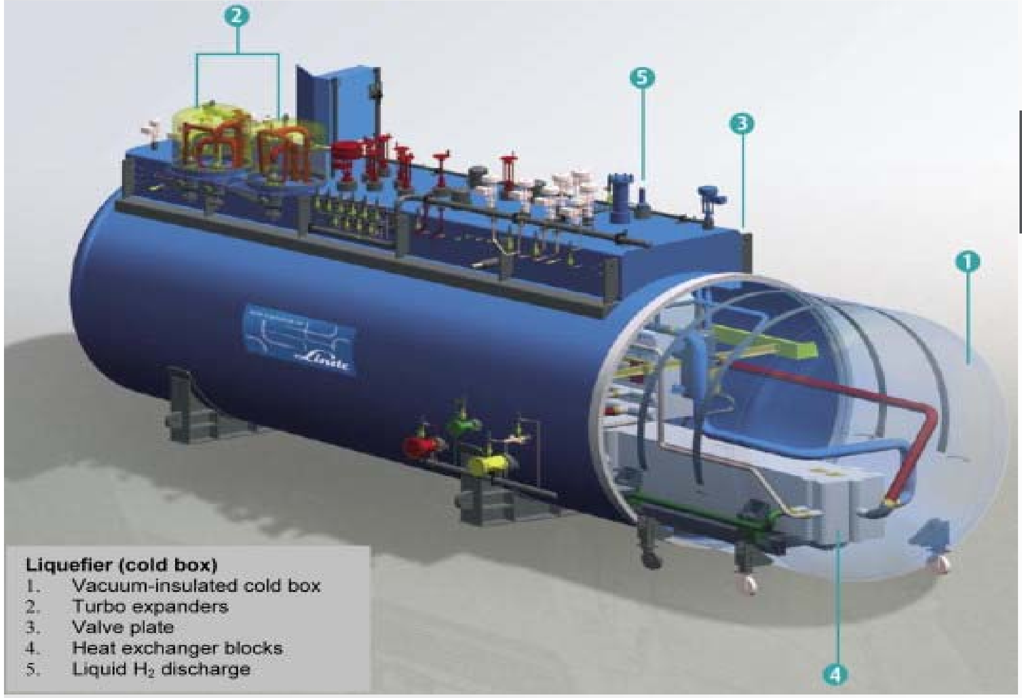
3) Next steps

Hydrogen Production Systems

- Multiple methods of hydrogen production
- Various balance of plant components



International Journal of Hydrogen Energy Volume 35, Issue 10 2010 4524 - 4533

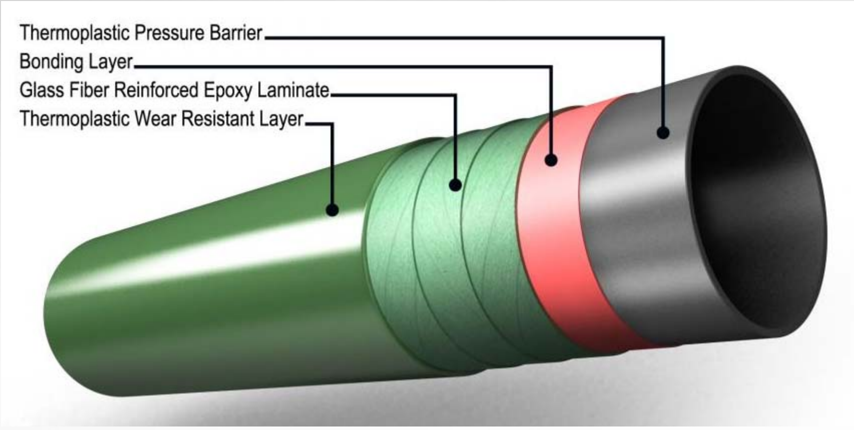


- Thermal and pressure variations throughout the production process
- Chemical compatibility with materials depending on the type of production feedstock

Hydrogen Transmission and Distribution

- Transmission Pipelines
- High Pressure Tube Trailer

Lincoln Composites



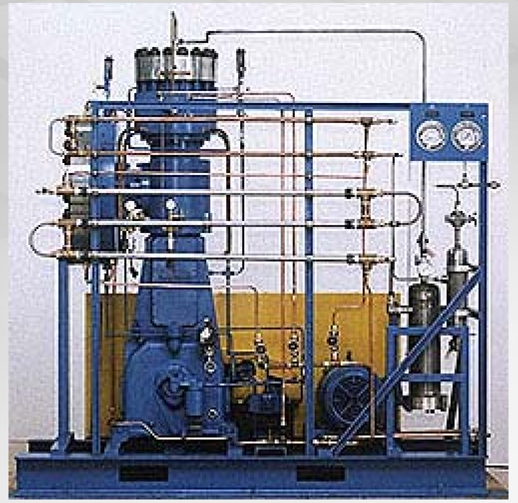
www.Fiberspar.com

- Liquefied Hydrogen (-253°C)
  - super-insulated, cryogenic tank trucks
  - High energy density transportation

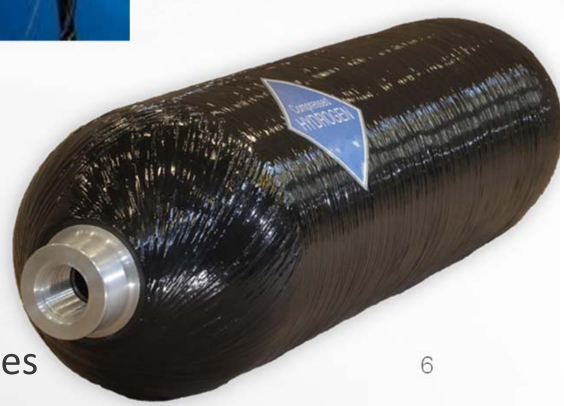
International Journal of Hydrogen Energy
Volume 35, Issue 10 2010 4524 - 4533

Hydrogen Delivery

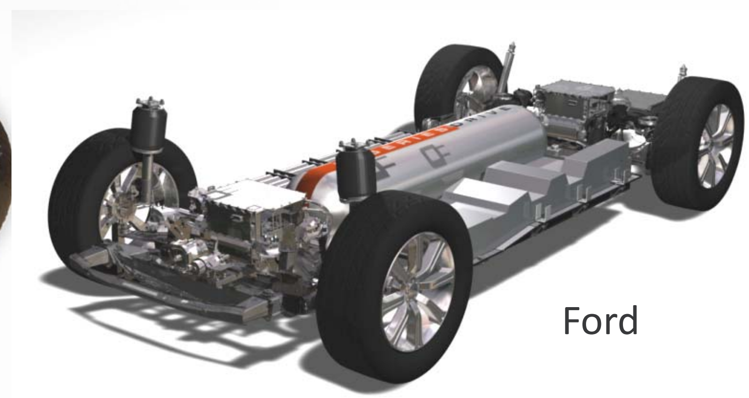
Pacific Northwest
ATIONAL LABORATORY
Proudly Operated by Battelle *Since 1965*



- Hydrogen compressors at the delivery station
- Hydrogen delivery systems to end use vehicles
- Quick fill rates
- High pressure dispensing to pressure vessels
- Cryogenic dispensing systems to cryo-compressed or cryo-adsorbent



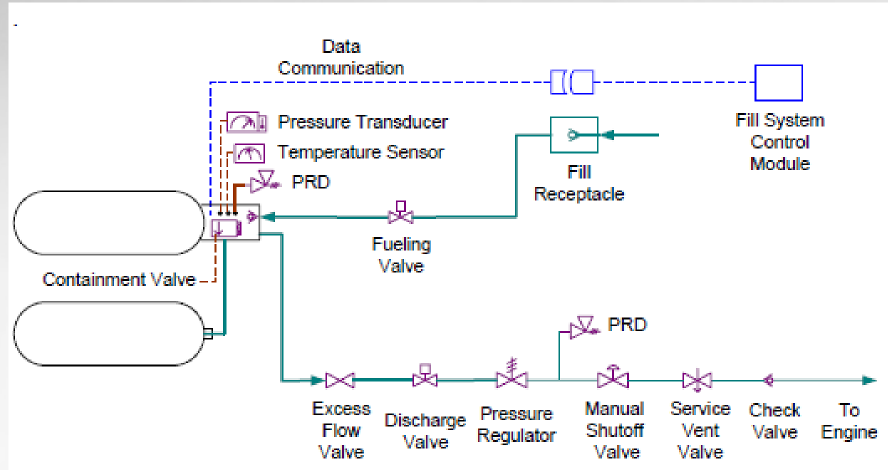
Lincoln Composites

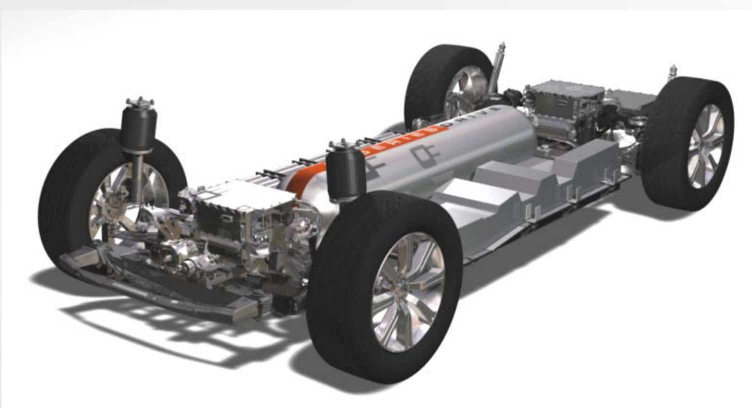


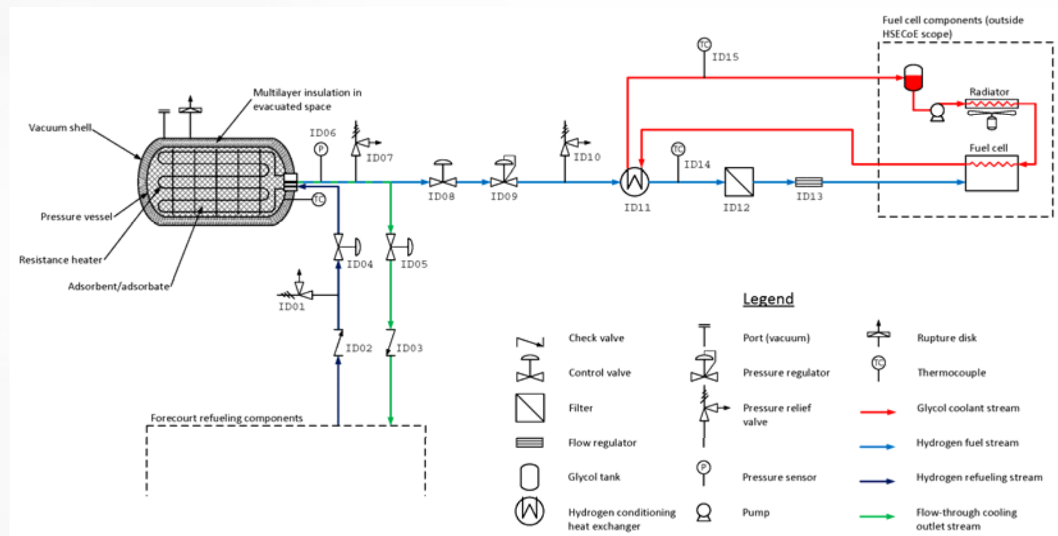
Ford

End User

- Compressed Hydrogen
  - 35 and 70 MPa
- Cryo-compressed
  - 20-27 MPa @ ~80K
- Cryo-adsorbent
  - 6-10 MPa @ 40-80K
- Storage materials
  - ammonia boranes, sodium and lithium alanates, and alanes

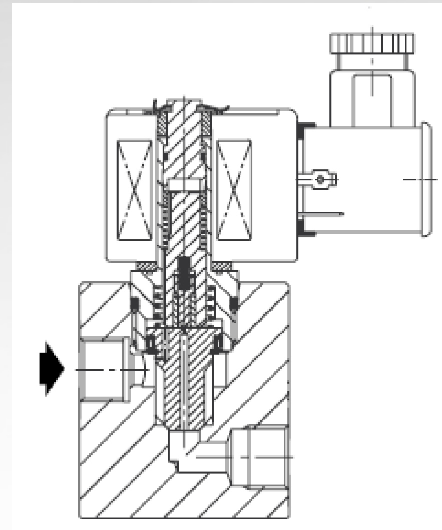


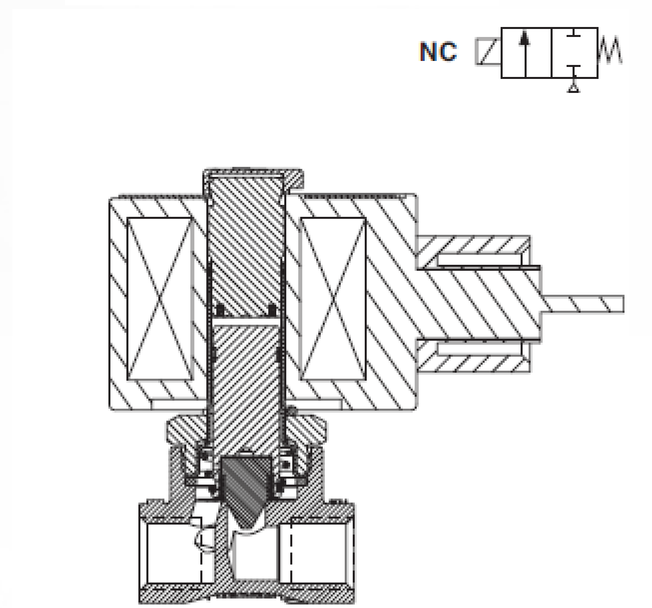


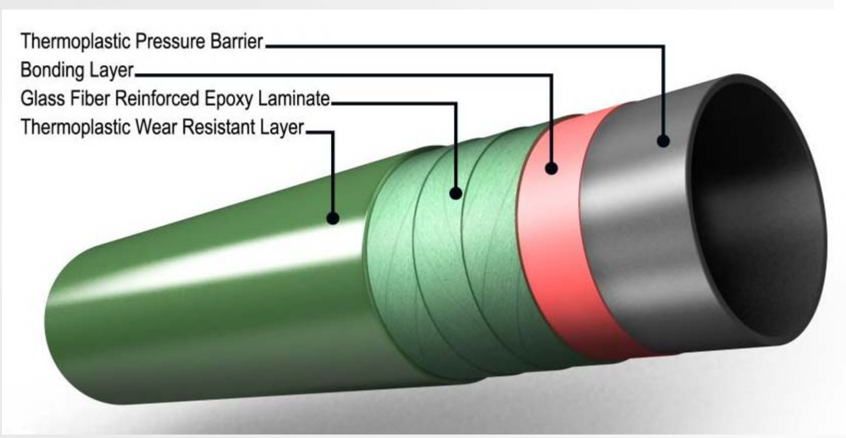


Common themes in the hydrogen system

- Balance of plant components
  - Valves
    - Valve seats
    - Stem seals
  - Regulators
  - Seals
- Pipe and tank liners







www.Fiberspar.com

Automotive versus Infrastructure

Pacific Northwest NATIONAL LABORATORY
Proudly Operated by Battelle Since 1965

- Components have different testing requirements
  - Automotive has aggressive use environments
    - Vibration
    - Impact
    - High reliability
    - High cycling
    - Chemical (road salts, oils, fuels)
    - Weight and volume sensitive
    - Others?
  - Infrastructure
    - Static system
    - High reliability
    - Continuous operations
    - Erosion from continuous flows?
    - Limited valve use
    - Low cycling

Hydrogen use conditions

- Pressures up to 100 MPa
- Temperatures between 20 and 423K (-253°C to 150°C)
- Hydrogen flow rates vary based on whether in production or delivery to the fuel cell
- Compressed Hydrogen
  - 35 and 70 MPa
- Cryo-compressed
  - 20-27 MPa @ ~80K
- Cryo-adsorbent
  - 6-10 MPa @ 40-80K
- Storage materials
  - ammonia boranes, sodium and lithium alanates, and alanes
  - Exo and endothermic systems
  - Hydrogen impurities (ammonia, diborane, hydrazine)

Polymer/elastomer and composites compatibility?

Pacific Northwest NATIONAL LABORATORY
Proudly Operated by Battelle Since 1965

- Very little information available for decision making
- There are common polymer types that appear to be used with balance of plant components
- Pressure vessel and piping liner materials are primarily HDPE, others have been used
- Polymers are much more sensitive to temperature than metals
- Pressure and hydrogen concentration can impact polymer properties and permeation

Polymer/elastomer and composites compatibility?

Polymers/elastomers

- Durability and mechanical integrity
  - Static or dynamic loading
  - Variable temperature
- Stability under high hydrogen concentration
- Permeation rates as function load and environmental conditions

Composites

- Multi-material systems
- Mechanical reliability
- Continuous service life with pressures up to 100 MPa

Hydrogen Storage Engineering Center of Excellence BOP Library

Pacific Northwest NATIONAL LABORATORY

Proudly Operated by Battelle Since 1965

Check Valves	10/11/2011 8:17 AM	File Folder
Composite Fiber	10/11/2011 8:17 AM	File Folder
Composite Resin	10/12/2011 9:11 AM	File Folder
Control Valves	10/11/2011 8:17 AM	File Folder
Fill Port Connections	10/7/2011 12:46 PM	File Folder
Filters	10/11/2011 8:17 AM	File Folder
Flow Controllers	10/11/2011 8:17 AM	File Folder
Fluid Pumps	10/11/2011 8:17 AM	File Folder
Gas Pumps	10/11/2011 8:17 AM	File Folder
Heat Exchangers	10/11/2011 8:17 AM	File Folder
Heat Transfer Fluids	10/12/2011 8:13 PM	File Folder
Heaters	10/11/2011 8:17 AM	File Folder
Insulation	10/11/2011 8:17 AM	File Folder
Pressure and Temperat...	10/11/2011 8:17 AM	File Folder
Pressure Regulators	10/11/2011 8:17 AM	File Folder
Pressure Relief Devices	10/11/2011 8:17 AM	File Folder
Pressure Vessels and C...	10/11/2011 8:17 AM	File Folder
Tank Liner Materials	10/11/2011 8:17 AM	File Folder
Tubing	10/11/2011 8:17 AM	File Folder

	Mass [kg]	Vol [L]
Insulated H2 tubing	0.240	1.500
H2 wetted tubing	0.600	4.500
Solenoid valves	2.025	1.575
Manual shut-off valves	2.025	1.575
Check valves	0.390	1.440
Pressure regulator	1.090	0.410
Flow controller	2.200	0.110
Filter	0.200	0.001
Temperature sensor	0.400	0.040
Burst Disk	0.100	0.010
Vacuum Port	0.100	0.010
Pressure gauges	0.440	0.100
H2 Pressure sensor	0.004	0.040
Micro-Combustor HX	1.370	0.654
Rubber tubing	1.830	3.420
FC coolant	2.400	0.000
Hose clamps	0.084	0.002
FC coolant bypass	0.680	0.390
Insulation	0.200	2.000
H2 fittings	2.000	0.200
Temperature sensor	0.452	0.002
Insulated H2 tubing	0.240	1.500
Manual shut-off valves	2.025	1.575
Check valves	0.260	0.960

Polymers identified from hydrogen BOP components

Materials for Hydrogen Components

Pacific Northwest
[partially hidden: …ORATORY]
[partially hidden: …attelle] *Since 1965*

Use	Material Type	Check Valves	Control Valves	Tanks and Pipes
Seals	Viton	x	x	
	Buna-N	x	x	
	Teflon	x	x	
	EPR	x	x	
	Fluorosilicone	x		
	Silicone	x		
	Neoprene	x		
	PEEK	x	x	
Pistons	PEEK	x	x	
Seats	Nylatron		x	
	Vespel		x	
	PCTFE		x	
Containment/pipes	Epoxy			x
	Vinylester			x
	Fiberglass			x
	Polyaramide (Kevlar)			x
	Carbon Fiber			x
	HDPE			x
	PPS			x

Kevin Simmons, PNNL 509-375-3651, kevin.simmons@pnnl.gov

Important Material Property Effects on Compatibility

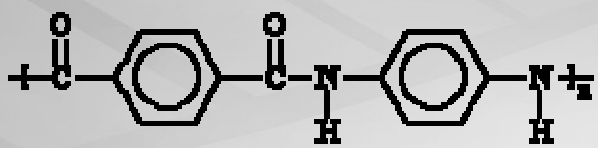
Polymers/Elastomers

- Permeability
- Amorphous vs semi-crystalline
- Glass transition temperature
- Molecular orientation
- Molecular mass
- Plasticizers

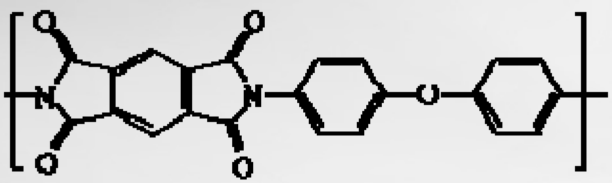
Composites

- Cross-link density
- Glass transition temperature
- Interfacial adhesion
- Fillers
- Fiber type
- Quality of composite
  - Porosity
  - Fiber wet out

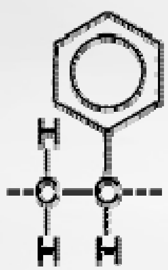
Common Polymer Structure



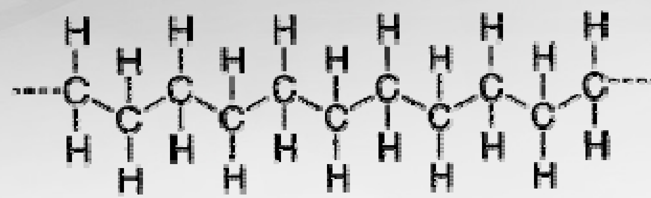
Polyamide (Kevlar)



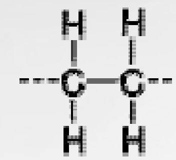
Polyimide (Kapton)

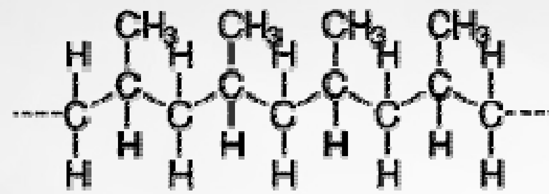


PS

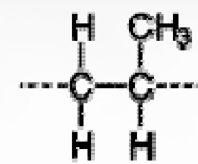


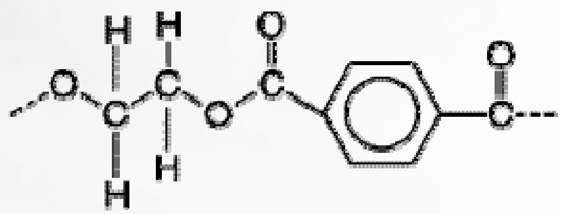
Polyethylene



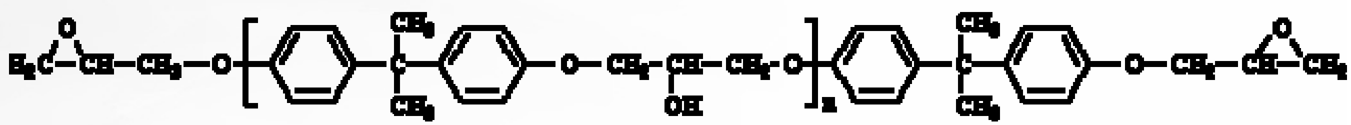


Polypropylene



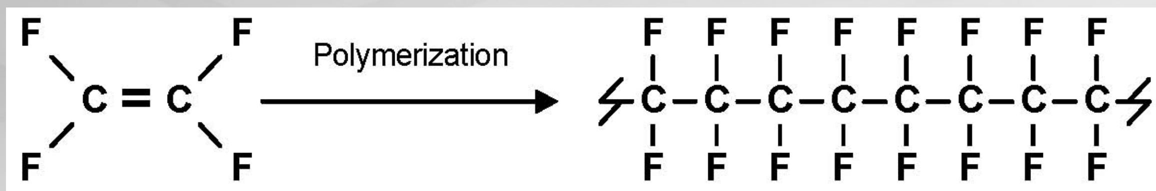


Polyethylene Terephthalate

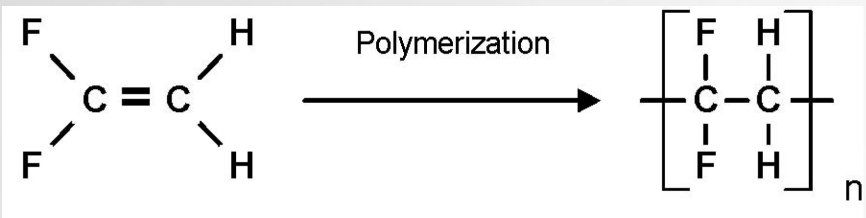


Epoxy

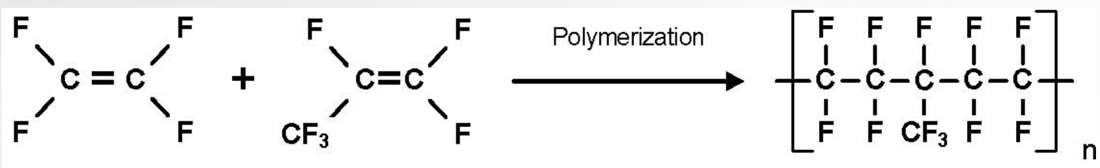
Fluoropolymers



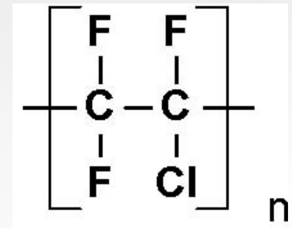
Tetrafluoroethylene PTFE



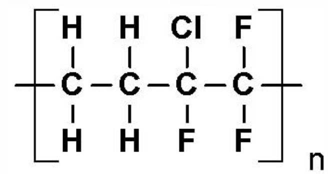
Vinylidene fluoride PVDF



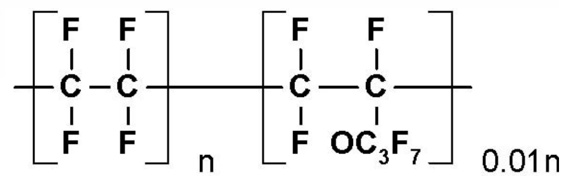
Tetrafluoroethylene Hexafluoropropylene *FEP*



PCTFE



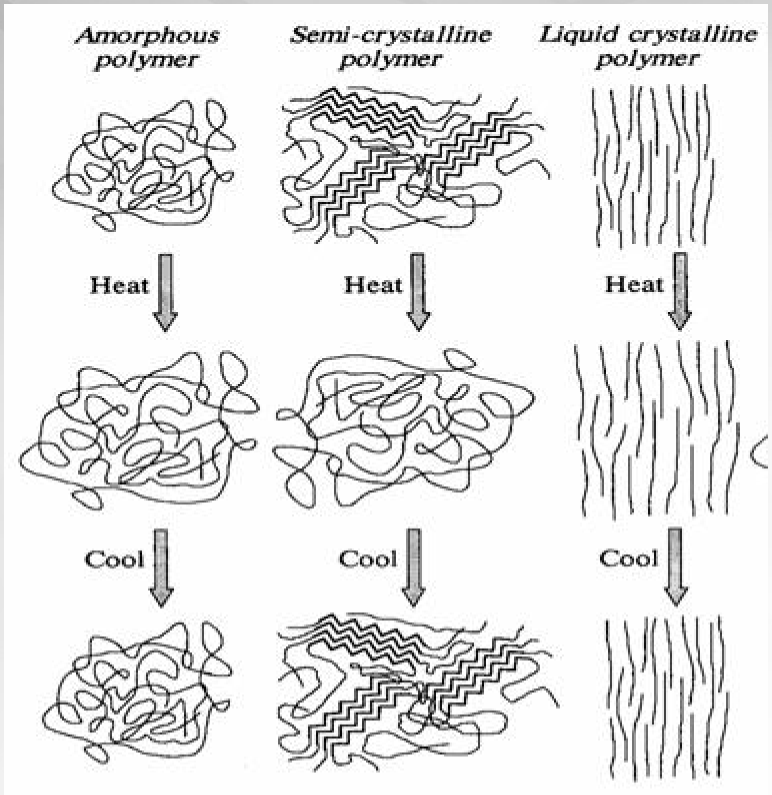
ECTFE



PFA

Polymer Structures

Pacific Northwest NATIONAL LABORATORY
Proudly Operated by Battelle Since 1965



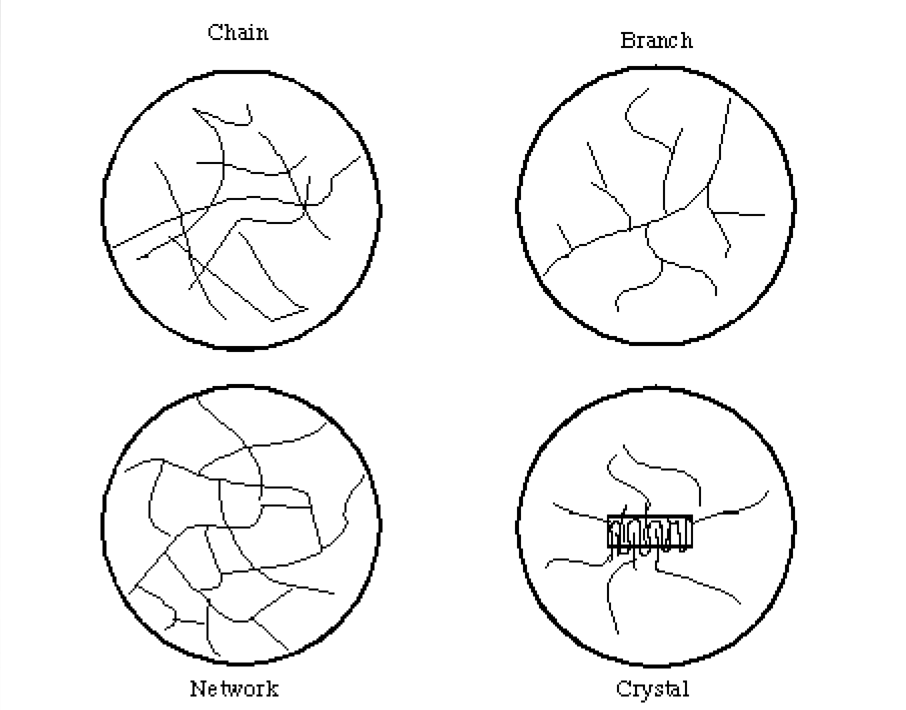


Figure 1.1 Polymer structures.

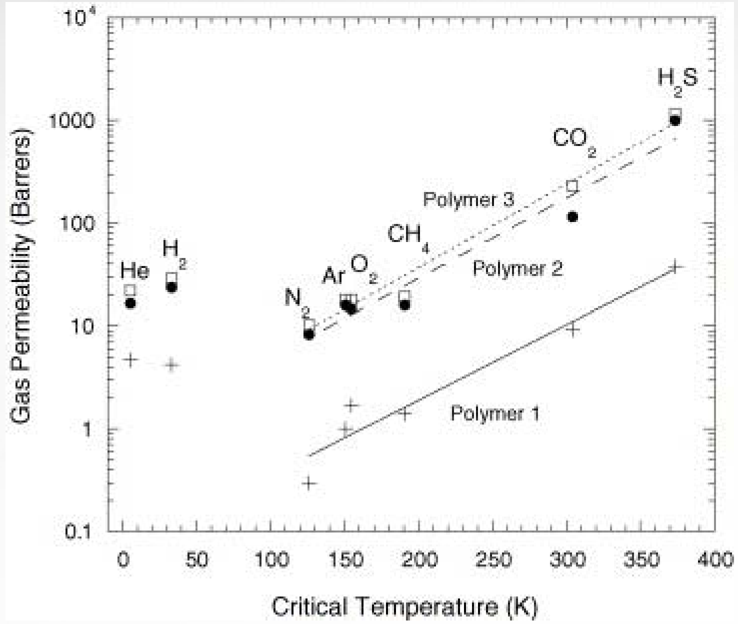
www.imold.com

www.mech.utah.edu/~rusmeeha/labnotes/degradation.html

Polymer morphology and free volume

Permeation is at the Heart

- Permeation is based on diffusion and solubility
- Permeation of hydrogen follows the Arrhenius rate
  - Colder temperature reduces permeation
- Free volume of the polymer is directly attributed to permeation
  - Amorphous polymers
  - Semi-crystalline
  - Cross-linked



Christopher et al., Journal of Membrane Science, V 253, Iss 1-2, 5 May 2005, Pages 243-249

Hydrogen Materials Compatibility Studies

Little is known about the effects of Hydrogen on Polymers.

Preliminary work

- Hydrogen exposure & decompression on amorphous polymers
- Preliminary results indicate that blistering does occur and is strongly dependent on viscosity/temperature
- Goal is to identify causes of blistering: viscosity, depth, solubility, diffusion, pressure, temperature, decompression time

Current & Future work

- Combinatorial approach to viscosity effect with thermal gradient stage
- Crystalline polymers

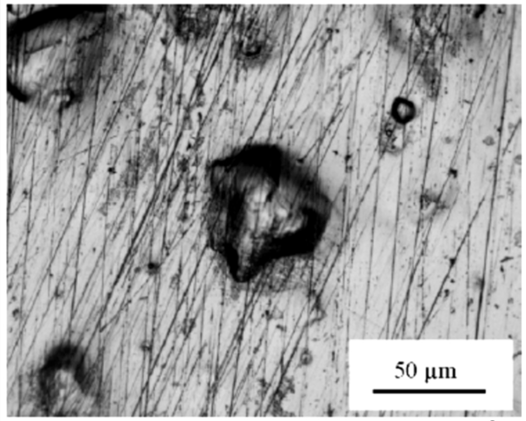
High-Pressure Hydrogen Test Chamber

- High Pressure Autoclave to simulate H-ICE environment.
- Variable hydrogen concentrations up to100 %
- Up to 5,000 psi max Hydrogen pressure
- Temperature -40 to 200°C
- *In-situ* thermal gradient stage

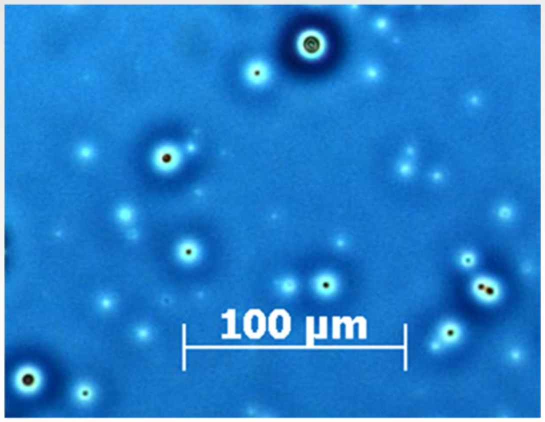
Hydrogen induced Polymer Blistering

Pacific Northwest NATIONAL LABORATORY
Proudly Operated by Battelle *Since 1965*

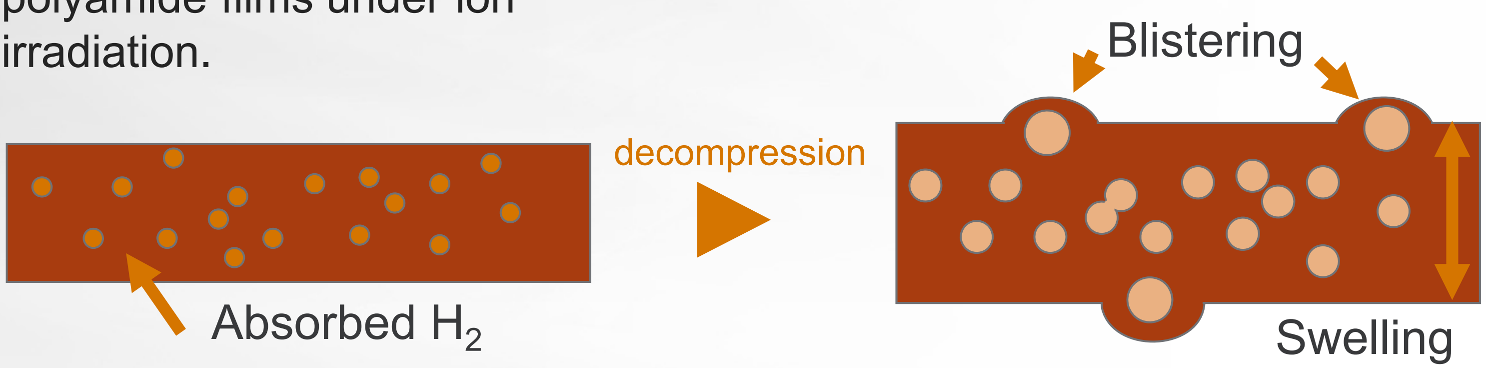
- Relatively high diffusivity or solubility of H_2 in polymers may lead to mechanical degradation or failure upon decompression.
- Hydrogen swelling and blistering common in metals.
- Blistering has been evidenced in polyamide films under ion irradiation.



H_2 Blistering in a Fe surface[3]



H_2 Blistering in Polystyrene



•C. S. Marchi *et al*, Sandia National Lab Technical Report (SAND2008-1163), 2008

•W. E. Wallace *et al* Nuc. Inst. & Methods in Phys. Res. B **103**, 435 (1995)

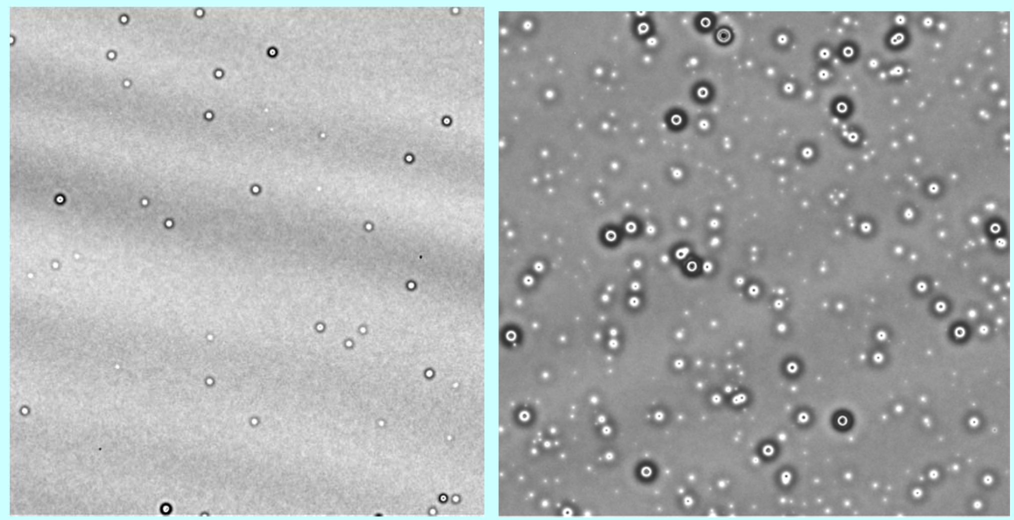
• Ren *et al*, Mater. Chem. Phys. **107**, 231, (2008)

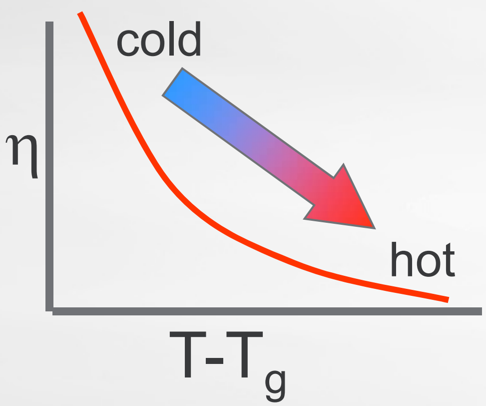
Temperature Effects on Blistering in High-Pressure H_2

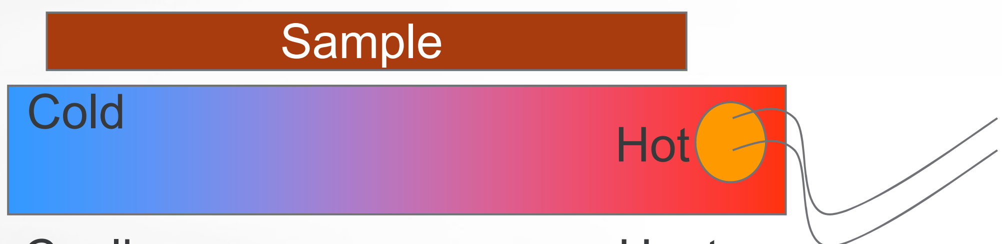
Pacific Northwest
NATIONAL LABORATORY
Proudly Operated by Battelle *Since 1965*

- Strong Viscosity Dependence
  - Blister Size & Density
- *In-Situ* thermal gradient stage allows combinatorial measurements of viscosity(η)

Viscosity/Temperature Dependence

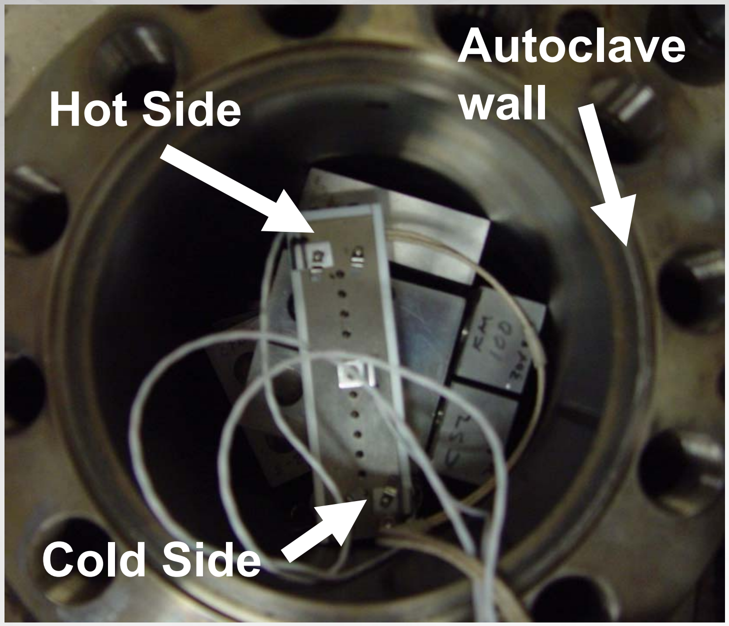


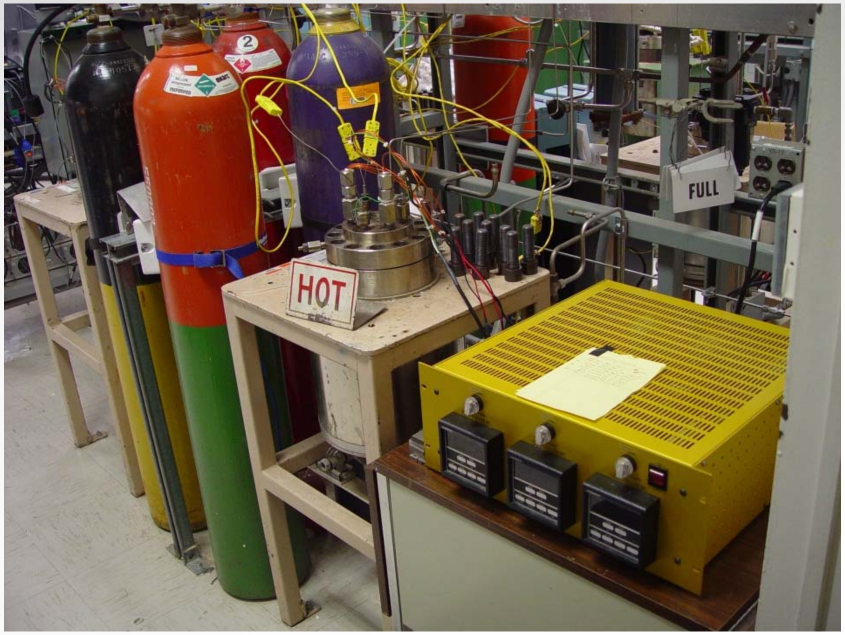




In-situ Thermal Gradient Stage for High-Pressure Hydrogen Charging

Pacific Northwest
NATIONAL LABORATORY
Proudly Operated by Battelle *Since 1965*





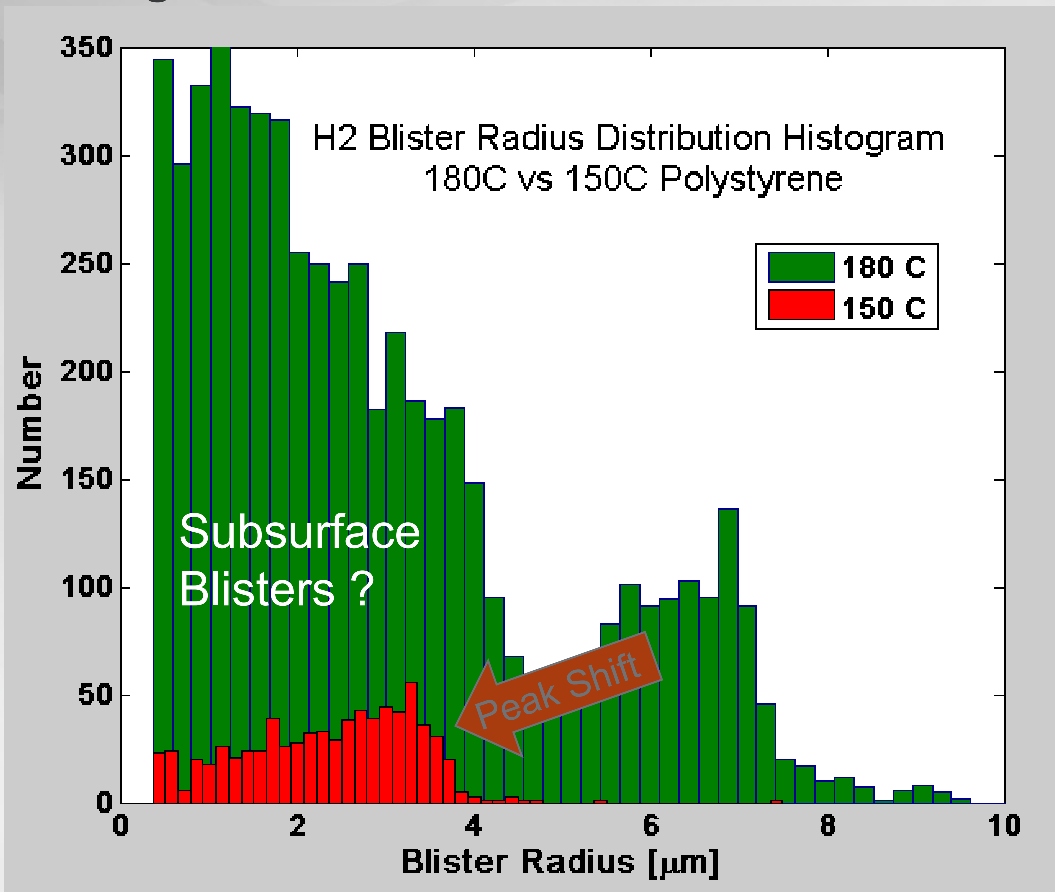
- In-situ thermal gradient stage allows combinatorial measurements of blistering as function of viscosity.
- Capable of 100 degree gradient

- PID control of hot end up to 200C yields large measurement range.
- Multiple temperature readouts.
- Under development.

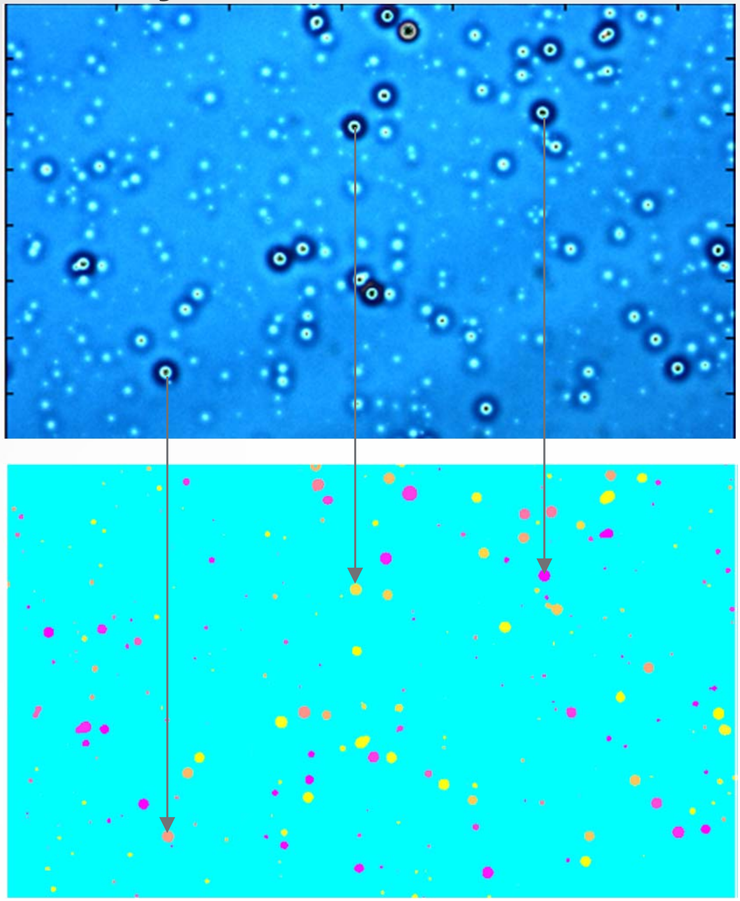
Image Analysis & Blister Size for different Temperatures

Pacific Northwest NATIONAL LABORATORY
Proudly Operated by Battelle Since 1965

Histograms for 150C & 180C



Identify & Measure Blisters



Hydrogen Materials Compatibility Studies: Summary & Future Work

Summary of preliminary work:

- Hydrogen induced damage does occur in polymers!
- Hydrogen induced blisters are clearly observed.
- Temperature/Viscosity is an important parameter to both blister size & density.
- Current goal to understand the effects of the different materials properties on the blistering.

Future work:

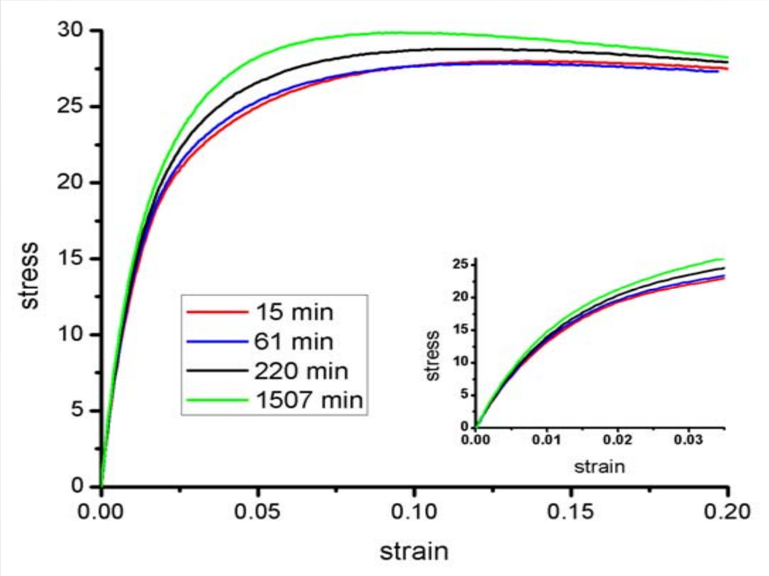
- In-situ combinatorial measurements of viscosity/temperature effect on blistering
- Extend work to crystalline/other polymer systems

PNNL's Accomplishments on Polymer Liner Hydrogen Compatibility

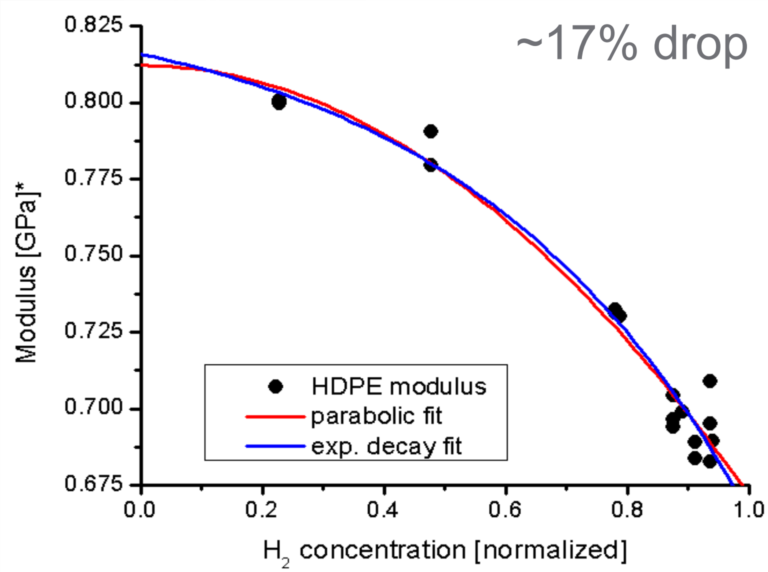
Pacific Northwest NATIONAL LABORATORY
Proudly Operated by Battelle *Since 1965*

- HDPE modulus & yield strength drop significantly when exposed to high pressure H_2
  - Highly dependent on amount of absorbed H_2 (high pressure = higher effect)
  - Ductility increases with amount of absorbed H_2
  - Modulus recovers as a function of time after exposure

Stress-Strain Curves HDPE H_2 Exposed



Modulus Drop & Recovery from H_2



HDPE modulus is negatively impacted as a function of H_2 absorption, but recoverable.

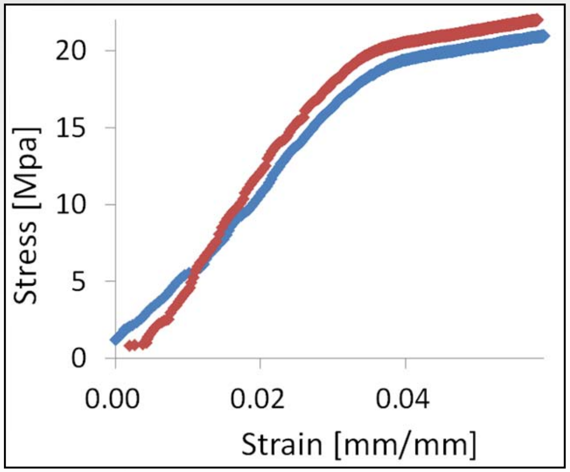
In-situ Testing

- PNNL has capability for in-situ testing of polymer materials in high pressure hydrogen
  - Tensile testing
  - Compression testing
  - Creep and recovery
  - Dynamic loading
    - Fatigue
    - Dynamic mechanical analysis
  - Hydrogen concentration control
  - Combinations of temperature, pressure, and concentration for broad design of experiment capability

Figure 1: (RIGHT) The high pressure hydrogen autoclave can accommodate up to 5” diameter x 10” height. (LEFT) A photograph of the partially completed in-situ tensile rig. LVDT is not shown.

PNNL Accomplishments on Polymer Tank Liner Hydrogen Compatibility

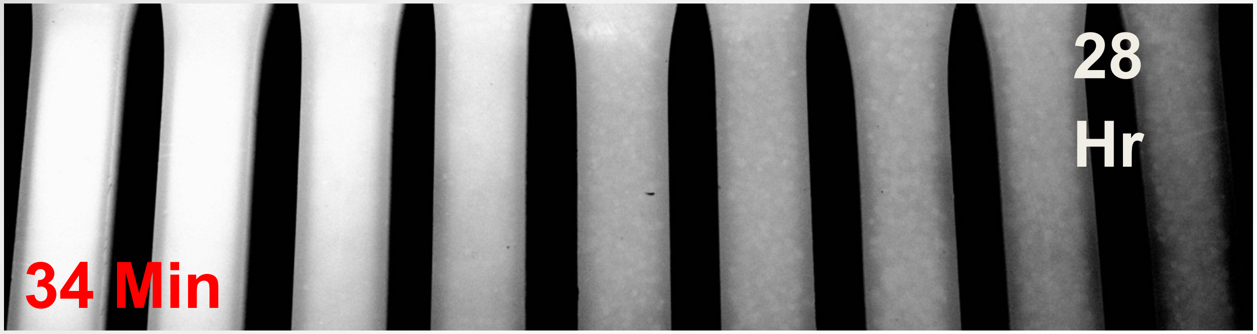
- In-situ tensile tester has been constructed and testing in 4,000 psi hydrogen
- All components work reproducibly in the high pressure environment
- Preliminary testing of stock HDPE samples shows decreased modulus under high pressure hydrogen
- Setup allows material tensile tests under hydrogen up to 5,000 psi
- Modifications for heating may be possible



Left: HDPE tensile samples before and after testing in 4,000 psi hydrogen. **Right:** Preliminary data from in-situ tensile rig. (Red) data is for HDPE pulled in air, and (blue) data is for an identical HDPE sample pulled in 4,000 psi hydrogen. Hydrogen data shows a lower modulus defined by the initial slope

LDPE Blistering studies

- LDPE tests show noticeable blistering

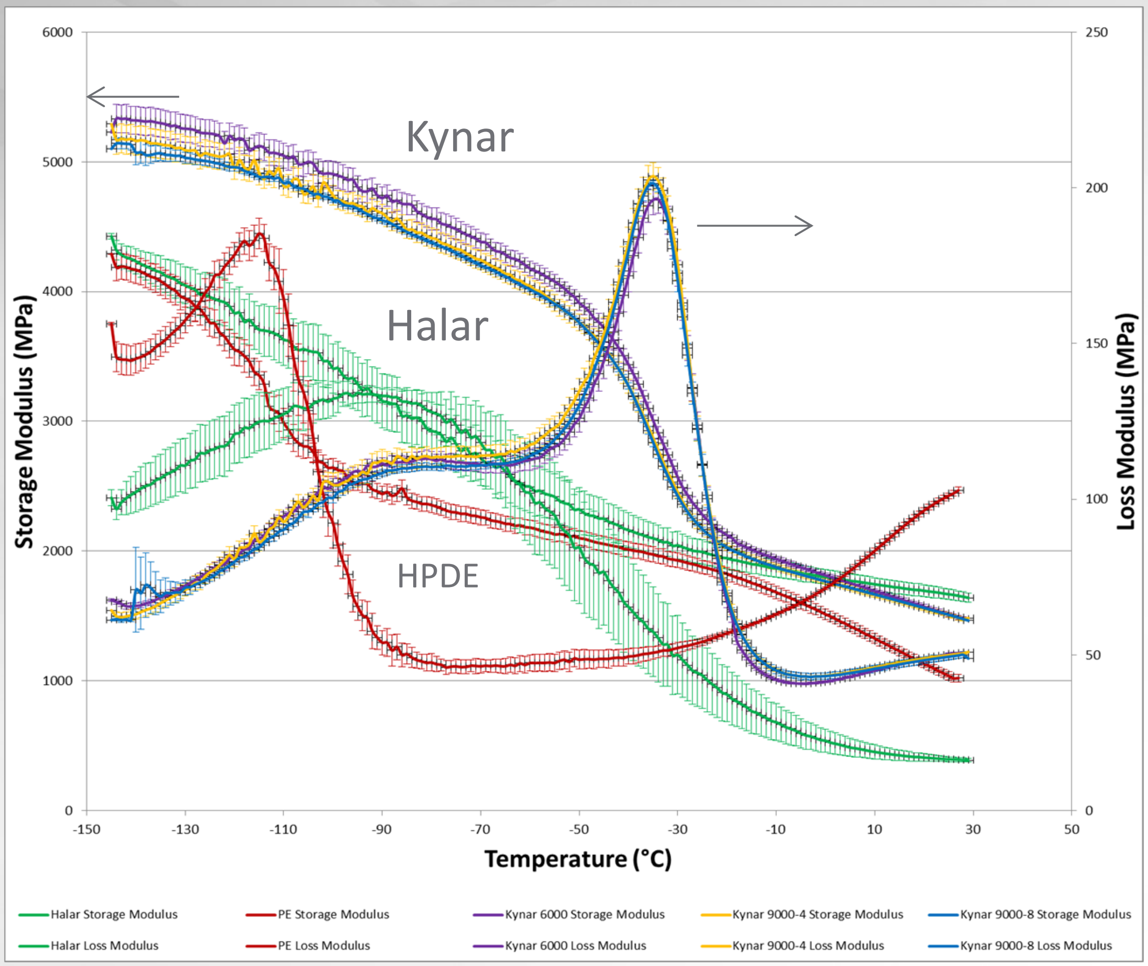


Graphic showing the progression of blistering formation in McMaster LDPE with time after removal from high pressure H2.

- Illustrates the degree of crystallinity increases diffusion
- Diffusion rates can increase by as much as six fold with a decrease in crystallinity from 90-30% as calculated by SRNL (M.C. Kane)

Dynamic Mechanical Analysis

Pacific Northwest NATIONAL LABORATORY
Proudly Operated by Battelle *Since 1965*



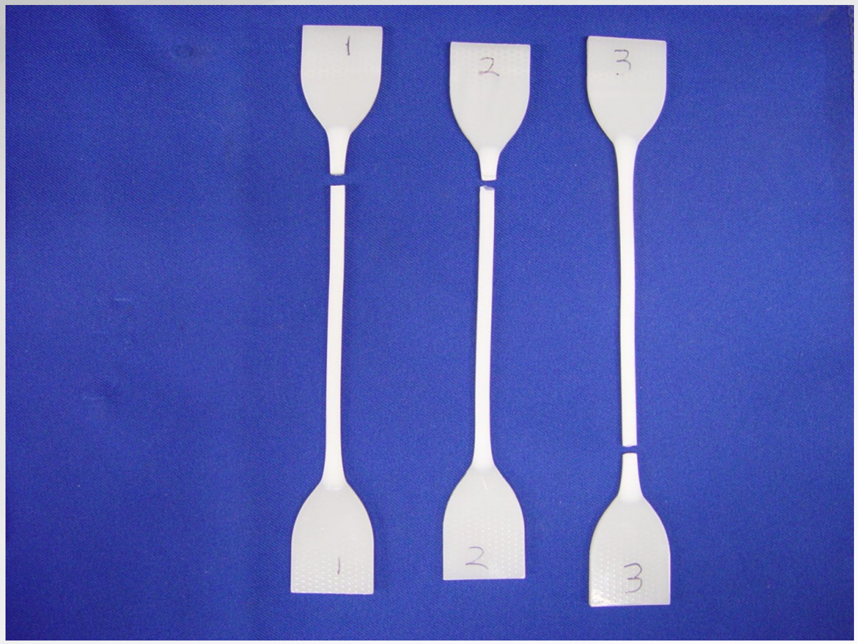
Sample	Storage Modulus 145°C (GPa)	Glass Transition T_g(°C)
HDPE	**4.29**	**-112.50**
Halar	4.43	77.30
Kynar 6000	5.23	33.63
Kynar 9000 44ccm	5.29	35.28
Kynar 9000 88ccm	5.10	34.93

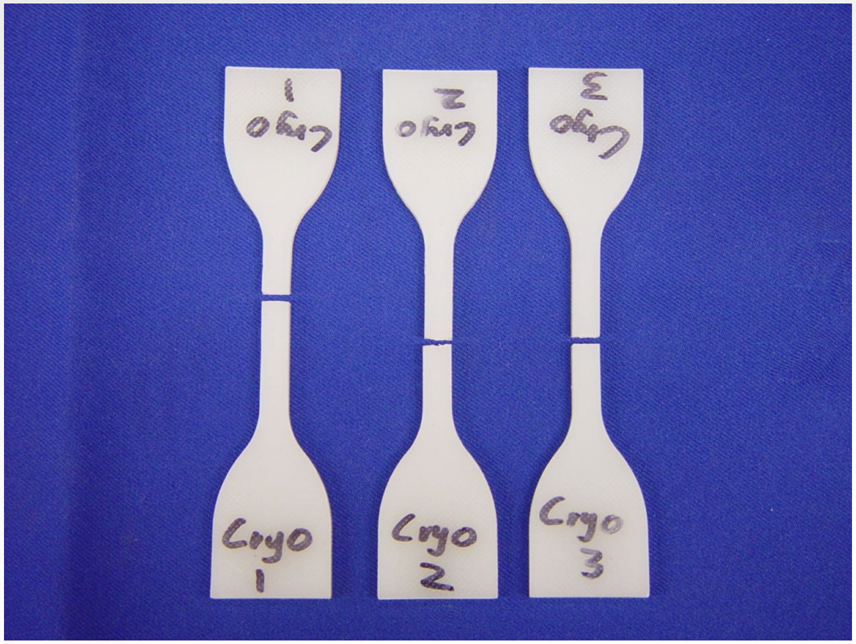
Halar and HDPE are the best performers to date at cryogenic temperatures

Halar

TS: 42 MPa
Modulus: 1.6 GPa
Elongation: 20%

TS: 143 MPa
Modulus: 4.4 GPa
Elongation: 4.5%





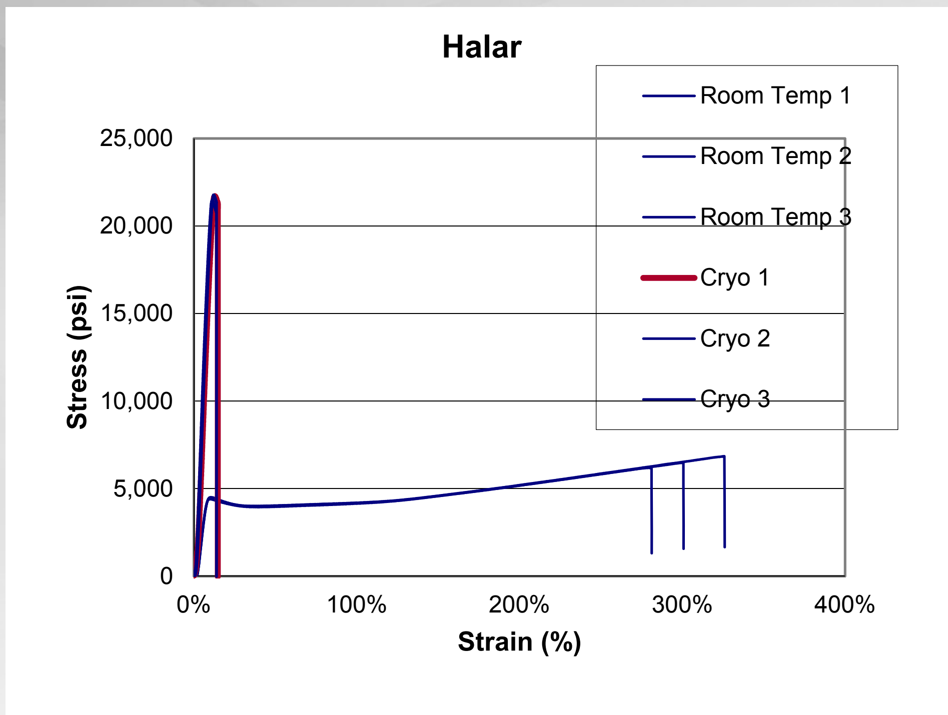
Room temperature

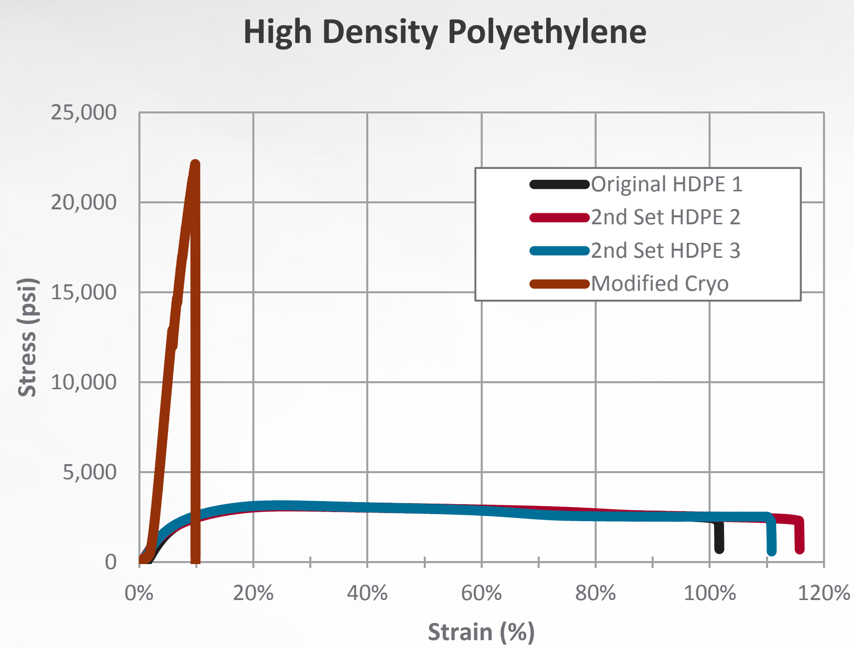
Liquid Nitrogen

Material Testing

Pacific Northwest
NATIONAL LABORATORY
Proudly Operated by **Battelle** *Since 1965*

Submersed in LN2
Temperature 80K

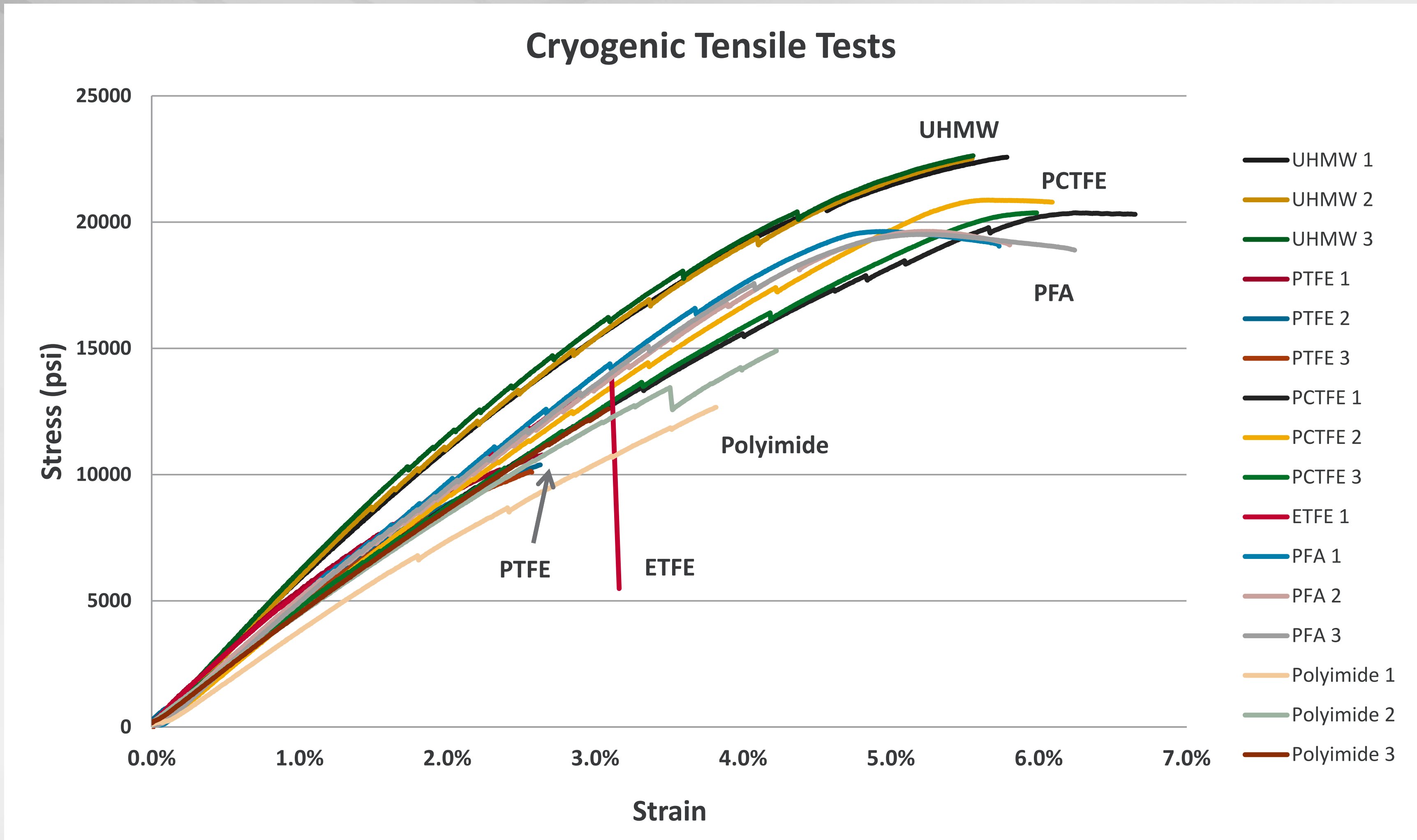




Significant changes in strength and modulus relative to temperature

Tensile Test Update

Pacific Northwest
NATIONAL LABORATORY
Proudly Operated by Battelle Since 1965



Composites

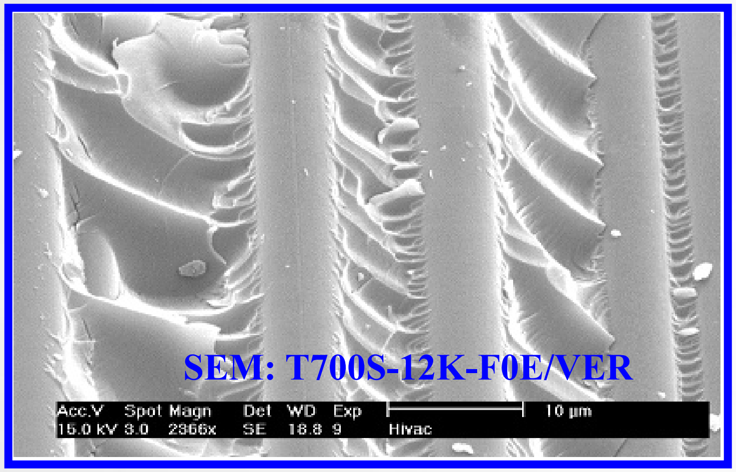
- Pressure vessels
  - Epoxy systems have higher permeation rates than the liner materials
- Piping
  - Buried pipe – impact, moisture, ect.
  - Above ground – UV, thermal effects
  - Different requirements
- Safety factors
- Glass fiber composites
  - Stress rupture consideration
- Common microcracking acts a pathway for hydrogen escape
- Trapped hydrogen between the liner and the composite causes the liner to push away from the pipe or the tank with depressurization
- Do liners grow with high pressure and creep?

Surface Modifications

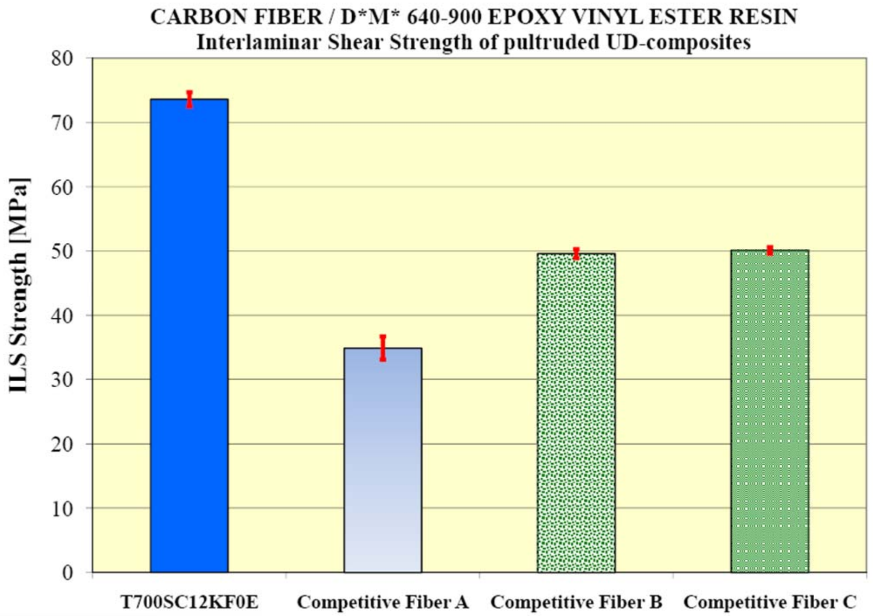
TORAYCA® Carbon Fibers:
Widest Range of Surface Treatments/ Sizings for Carbon Fibers

TORAYCA fibers are treated with various sizing agents to enhance the handleability and bonding characteristics with various resin systems. Below are the sizing types developed for TORAYCA fibers. Not all sizings are available with every fiber. Please see the data sheets for available sizings of a particular fiber.

Sizing Type	Resin System Compatibility
1	Epoxy
3	Epoxy
4	Epoxy, phenolic, BMI
5	General purpose: Epoxy, phenolic, polyester, vinyl ester
6	Epoxy
F	Designated for vinyl ester, compatible with epoxy



SEM: T700S-12K-F0E/VER

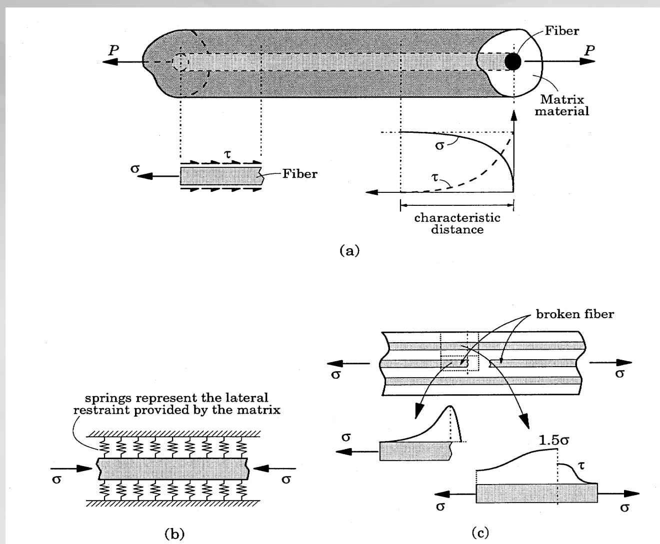


Surface Modifications Impacts

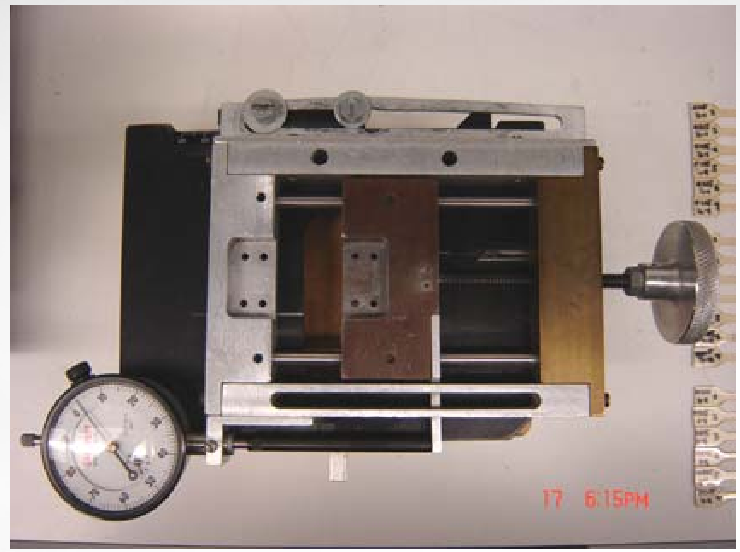
Pacific Northwest
NATIONAL LABORATORY
Proudly Operated by Battelle *Since 1965*

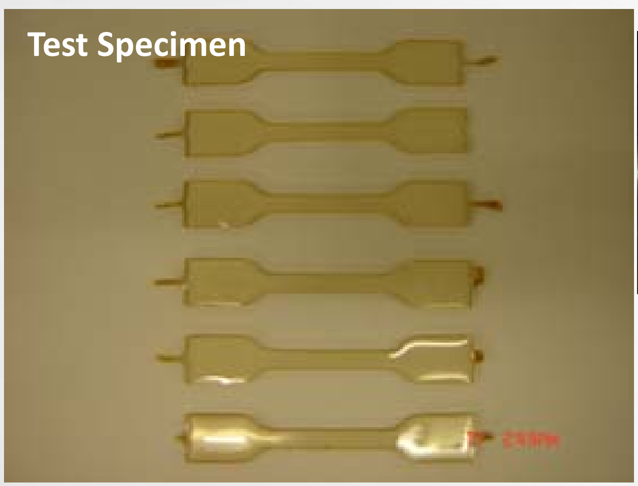
Single Fiber Fragmentation Test (SFFT) for adhesion analysis

Mechanics of Stress Transfer At Fiber Break



SFFT Fixture To Measure Interfacial Shear Stress (IFSS)





$$\text{IFSS:} \quad \tau = \frac{\sigma_f \times d}{2 l_c}$$

Next Steps

- Develop testing protocols for material evaluations
  - Pressure, temperature, and concentration
  - Accelerated testing protocol: Testing rates, fatigue frequency
- Determine hydrogen effects in polymers and elastomers, including aging, wear, and structural changes (creep, modulus, etc.)
- Determine the effects of high pressure on polymers/elastomers
  - Does pressure reduce or increase in permeation?
  - Does hydrogen act like a solvent?
- Define reliability
- Determine and define the limits on decompression rates at certain pressures to minimize damage to the system
- Determine composite pipe joining technology limitations on hydrogen leak rates
- Determine the limitation of adhesives and can they be effectively used
- Define standard design requirements
- Define the qualification protocols
- Define the operational protocols
  - Does operational protocol drive qualification?
- Develop a simple table to compare material properties based on the condition
  - What works and what doesn't?

Compatibility Test Terms

Pacific Northwest NATIONAL LABORATORY
Proudly Operated by **Battelle** *Since 1965*

- PDL Rating: Plastics Design Library, The assigned number represents the material's resistance to a reagent based on a baseline of '10' prior to exposure
- Tensile Modulus: The linear elastic component of a material before yielding. Used in determining brittleness or flexibility of a material
- Tensile Yield The point on a stress curve at which a material undergoes permanent deformation
- Flexural Modulus: The flexural elastic component of a material before yielding. Also used to determine brittleness or flexibility
- Flexural Peak Stress: The resistance to bending of a material when subjected to flexural stress
- Static Contact Angle: Represents the difference in the surface energies of twosurfaces (water and plastic surface), the angle increases as the hydrophobic nature of the material surface increases

PDL Resistance Rating Guide

Weighted Value	Weight Change*	Diameter; Length Change*	Thickness Change*	Volume Change*	Mechanical Property Retained**	Visual/ Observed Change***
10	0-0.25	0-0.1	0-0.25	0-02.5	≥97	no change
9	>0.25-0.5	>0.1-0.2	>0.25-0.5	>02.5-5.0	94 - <97	
8	>0.5-0.75	>0.2-0.3	>0.5-0.75	>5.0-10.0	90 -<94	
7	>0.75-1.0	>0.3-0.4	>0.75-1.0	>10.0-20.0	85 -<90	Slightly discolored, slightly bleached
6	>1.0-1.5	>0.4-0.5	>1.0-1.5	>20.0-30.0	80 -<85	Discolored yellows, slightly flexible
5	>1.5-2.0	>0.5-.75	>1.5-2.0	>30.0-40.0	75 -<80	Possible stress crack agent, flexible, possible oxidizing agent, slightly crazed
4	>2.0-3.0	>.75-1.0	>2.0-3.0	>40.0-50.0	70 -<75	Distorted, warped, softened, slight swelling, blistered, known stress crack agent
3	>3.0-4.0	>1.0-1.5	>3.0-4.0	>50.0-70.0	60 -<70	Cracking, crazing, brittle, plasticizer, oxidizer, softened, swelling, surface hardened
2	>4.0-6.0	>1.0-1.5	>4.0-6.0	>60.9-90.0	50 -<90	Severe distortion, oxidizer and plasticizer deteriorate
1	>6.0	>.0	>6.0	>90.0	0 -<50	Decomposed
0					0	Solvent dissolved, disintegrated

Source: PDL Handbook Series: Chemical Resistance Vo. 1 - Thermoplastics

Example and Footnotes to PDL Resistance Rating Guide

Pacific Northwest
NATIONAL LABORATORY
Proudly Operated by **Battelle** *Since 1965*

Title: Chemical Resistance of Plastics and Elastomers (3rd Electronic Edition)

Table: Polyethylene, HDPE

no.	exposure medium	conc. (%)	temp. (°C)	exposure time (day)	strain (%)	PDL rating	resistance note	volume change (%)
2288	Hydrogen		60	60		8	resistant	<3
2283	Hydrogen	100	60			8	resistant, no indication that serviceability would be impaired	

* **All values are given as percent change from original.**

** **Percent mechanical properties retained include tensile strength, elongation, modulus, flexural strength, and impact. If the % retention is greater than 100%, a value of 200 minus the % property retained is used in the calculations.**

*** **Due to the variety of information of this type reported, this table can be used only as a guideline.**

Source: PDL Handbook Series: Chemical Resistance Vo. 1 - Thermoplastics