Lifecycle Verification of Polymer Liners in Storage Tanks

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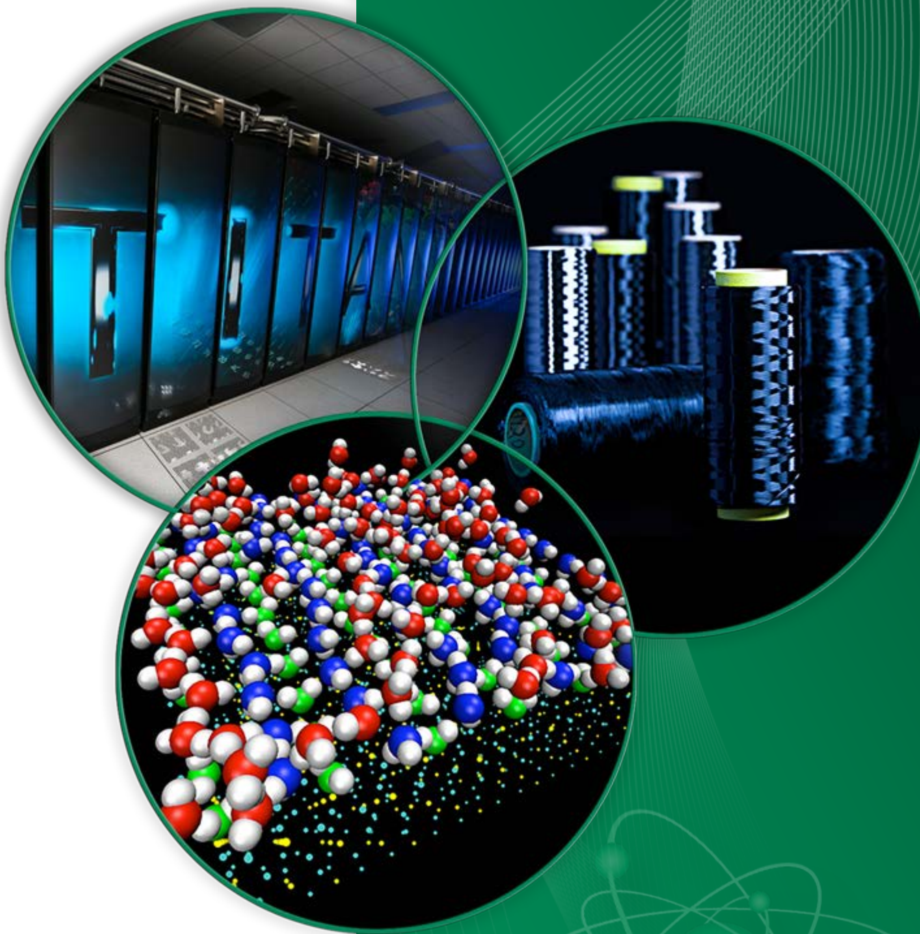

Annual Merit Review
Crystal City, VA
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Project ID #: ST053

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Overview

Timeline

- Start: June 2008
- Finish: Oct 2013*

Budget

- Total project funding
  - DOE: $750k
- Funding received in FY12: $175k
- Funding for FY13: $150k

*Project continuation & direction determined annually by DOE

Barriers

- Barriers
  - Durability of on-board storage systems – lifetime of at least 1500 cycles
  - Lack of tank performance data and understanding of failure mechanism
- Targets
  - Permeation and leakage: Loss of useable H_2 (g/h/kg H_2): FY 2017: 0.05; Ultimate: 0.05

Partners & Collaborators

- Manufacturers of Type 4 storage tanks

Relevance

Project goal: Perform thermal cycle durability qualification measurements on polymeric tank liner specimens and assess the ability of liner materials to maintain required hydrogen barrier performance.

Technical Barriers

D. Durability of on-board storage systems

G. Materials of construction

M. Lack of tank performance data and understanding of failure mechanisms

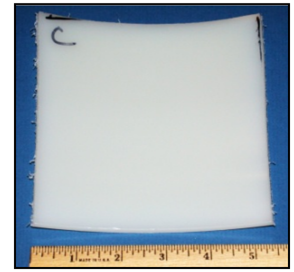
Approach

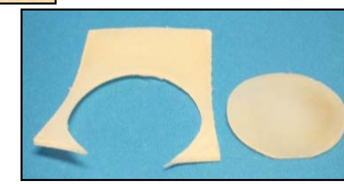
- Devise and publicize test procedure for temperature cycling tank liner specimens, establish standardized test methods, and provide durability data on various polymers for manufacturers of Type 4 storage tank systems
- Use permeability data to develop understanding of mechanisms for changes in liner permeability during thermal cycling
- Continue developing test methodology for assessing liner behavior and durability with the liner attached to the composite reinforcement shell

FY 2013 Tasks and Milestone

Date	Milestones	Progress Notes
April 2013	Publication of test protocol and with results in peer-reviewed journal	Protocol demonstrated; expect to publish results of tests on five tank liner polymers by end of FY 2013
Sept 2013	**SMART Milestone:** Complete thermal cycling and permeation measurements on new set of polymer specimens at both 350 and 700 bar, and use data to assess ability of tank liners to retain a steady state hydrogen discharge rate that does not exceed 110% of the 75 Ncc/min permeation requirement of SAE J2579 § 5.2.2.1.3, and report results	Two new tank liner specimens were obtained and we expect testing at 700 bar to be completed by the end of FY 2013

Technical Approach – Test Protocol

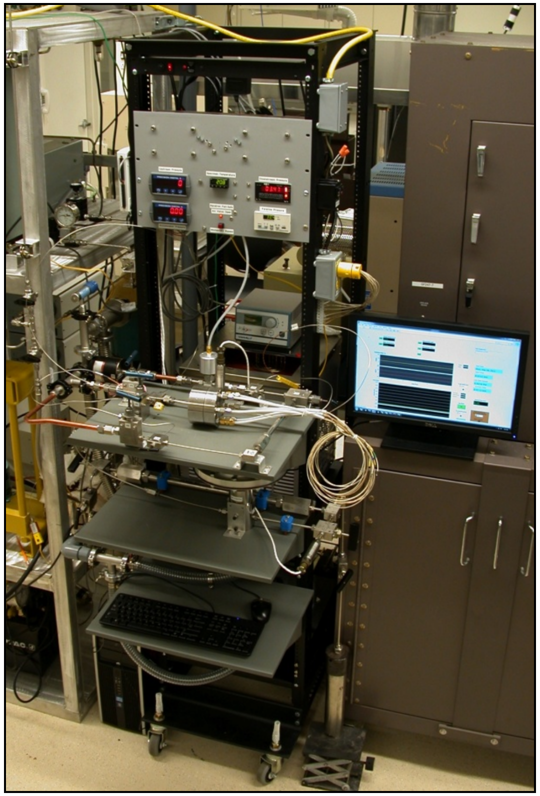




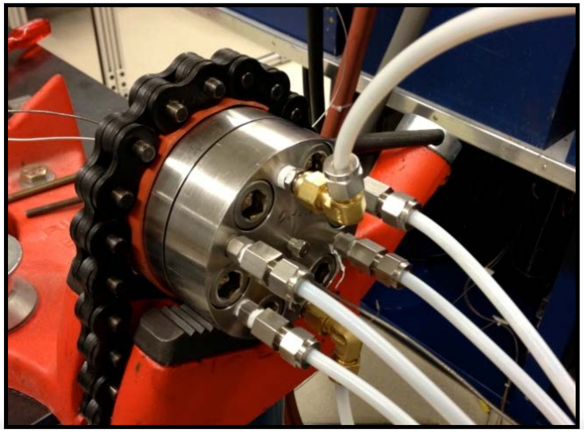
- Polymer specimens
  - Specimen discs prepared from tank liner sections
  - Each disc 5.7-cm dia. × approx. 1-mm thick (4.5-cm dia. area exposed to high-pressure H_2)
  - Prepared by lathe turning and wet sanding on low-pressure side
  - Liner interior (pristine surface) is exposed to high-pressure H_2
  - Larger specimen size provides faster, more accurate permeation measurements
- Temperature cycling protocol based on SAE J2579 § 5.2.2
  - 1500 temperature cycles, -40 to 85°C
  - Constant differential hydrogen pressurization: 350 or 700 bar
- Permeation rate measurements (pressure rise method)
  - Measure *P* at temperatures -40, -10, 30 and 85°C at intervals of 750 cycles (*i.e.*, at completion of 0, 750 and 1500 cycles)
  - Measure *P* at -40 and 85°C at completion of 250, 500, 1000 and 1250 cycles

Technical Approach – New apparatus

- Specimen pressure vessel
  - 316 SS bolted flanges, designed for 860 bar max working pressure
  - Specimen is sealed by compression in annular ring between pressure vessel flanges (10 cm^2 sealing area)
  - Vessel immersed in chilled bath (-40°C) of ethylene glycol/distilled water
  - Vessel is heated with six 300 W (1800 W total) immersible cartridge heaters



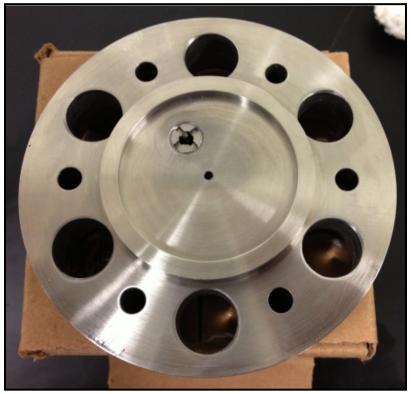
Temperature cycling apparatus



Assembled pressure vessel

Technical Approach – New apparatus

- Specimen pressure vessel
  - Specimen is differentially pressurized during temperature cycling, with high pressure on "upstream" side of disc, sub-atmospheric pressure on "downstream" side
  - Permeation measurements are performed without removing vessel from bath or specimen from vessel



Upstream flange, showing TC connection and gas inlet

Downstream flange with cartridge heaters and quartz support frit installed

Downstream flange with polymer specimen and metal foil seal folded over edge

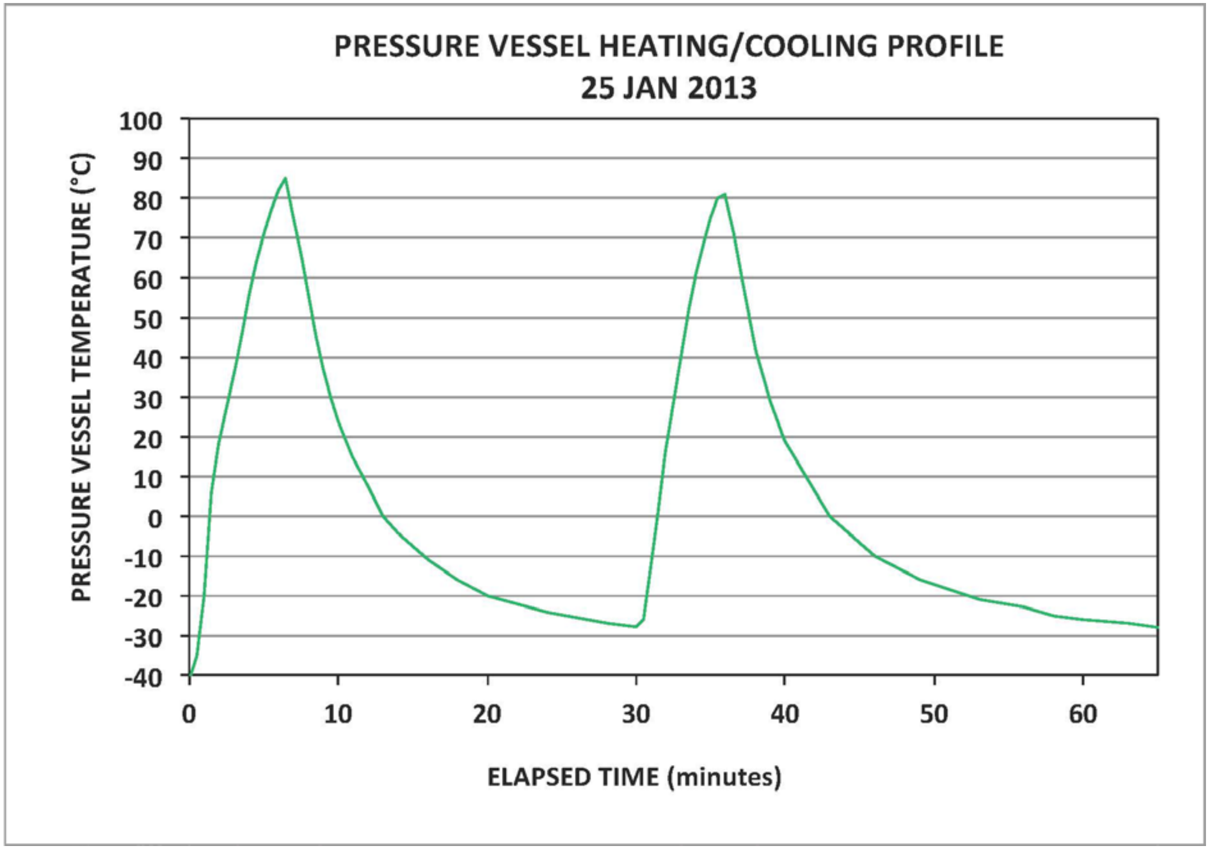
Progress – Workarounds and lessons learned

- In late FY 2012 apparatus was moved from lab space in Polymer Matrix Composites/Low Cost Carbon Fiber area to lab space in new chemical sciences building to alleviate power limitations and address safety concerns
- Prolonged temperature cycling runs now in progress following lengthy effort to resolve instrumentation and equipment problems
  - Cartridge heaters performed below spec, resulting in non-uniform heating of pressure vessel and excessive heat being added to low-temperature bath
  - Cooling power of refrigeration system in low-temperature bath decreases significantly below -20°C and was insufficient for withdrawing heat added to bath by heated vessel
  - Workarounds:
    - Modification of heating algorithm to reduce heat load
    - Addition of second refrigerated bath in series with primary bath to increase heat capacity and cooling power (in progress)
    - In planning stage – Replace viscous ethylene glycol solution used in bath with hydrocarbon-based heat transfer fluid

Progress – Workarounds and lessons learned

- High-pressure hydrogen regulator was discovered to be *not* hydrogen-compatible and was returned to factory for replacement of seals and gaskets
- Premature failure of thermocouple required disassembly of weldment and replacement
- Fluctuating pressure readings from high-pressure transducers has required the use of signal averaging until noise problem can be resolved
- RTD sensor inaccuracy in low-temperature bath required work-around to control stabilization of bath temperature

Progress – Temperature cycling in new apparatus



Heating interval is acceptable (20°C/min) but cooling interval was much longer than expected (~24 min) based on design calculations

Progress

- Additional liner materials obtained in FY 2013 through collaborations, and added to test matrix
  - Rotomolded HDPE
  - Blow-molded PET
  - Thermotropic liquid crystal polymer (TLCP)

Progress – Developed method for producing reliable high pressure seals

- A significant amount of trial and error is required to perfect the methodology for sealing each type of polymer due to
  - Differences between thermal expansion of polymer and SS vessel
  - Variations in polymer hardness, modulus and surface texture

Liner with smooth surface on inner surface

Compression seal performs well at all temperatures

Liner with dimpled or patterned inner surface

Compression seal leaks at low temperature extreme, requires use of metal foil

Polymer with large modulus

Hard, brittle, irregular surface makes it difficult to get a good high-pressure seal, even with foil

Progress – Developed method for producing reliable high pressure seal

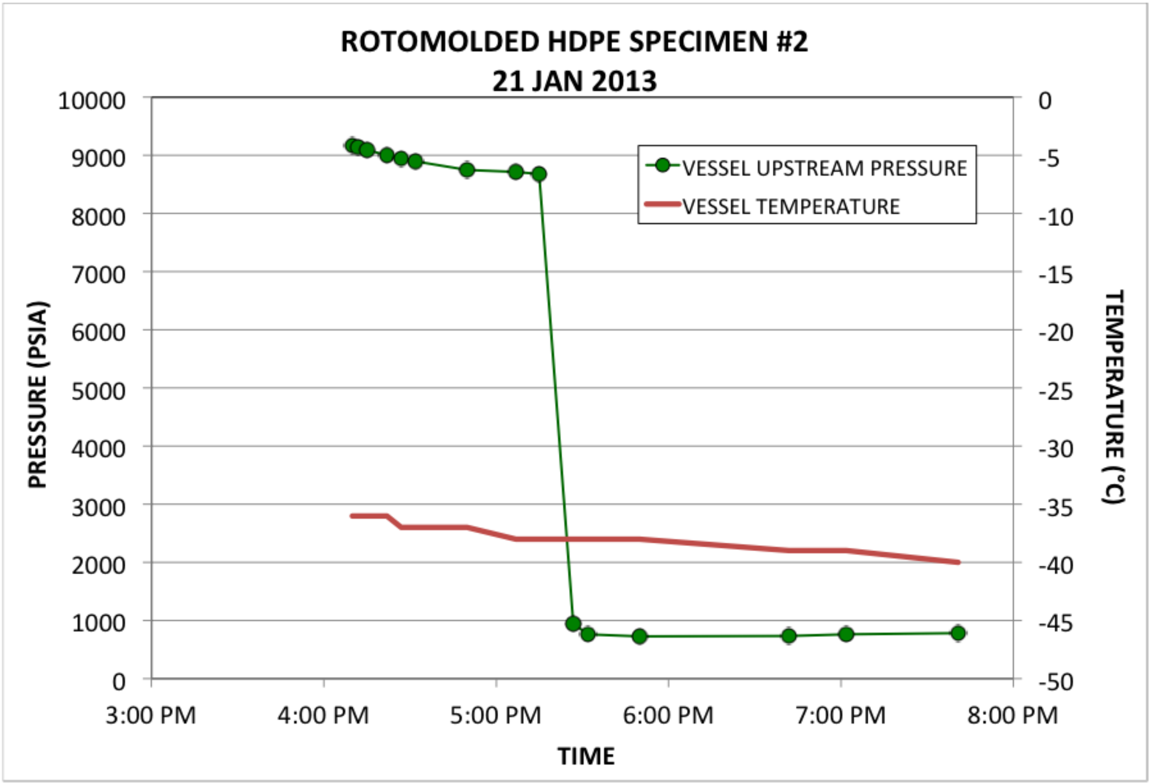
Each polymer requires a variation of the basic sealing methodology

- The harder the polymer or the more patterned the surface on the high-pressure side, the more challenging is the high-pressure seal
- The use of metal foils in a Bridgman-type seal design is critical to success
- Temperature cycling must be halted and the vessel removed from the low-temperature bath on occasion to retighten the flange bolts to compensate for plastic deformation of the polymer

Progress – Devised robust frits for specimen support in vessel

Rapid depressurization initiated by failure of specimen support frit in downstream flange

- Quartz frit was compressed and cracked by force applied by specimen surface
- Compressed frit allowed specimen to flex to the extent that the embedded thermocouple probe punctured the specimen



Gradual decrease in upstream pressure, followed by rapid depressurization event

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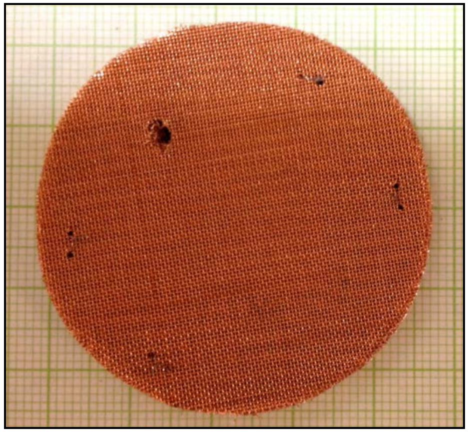
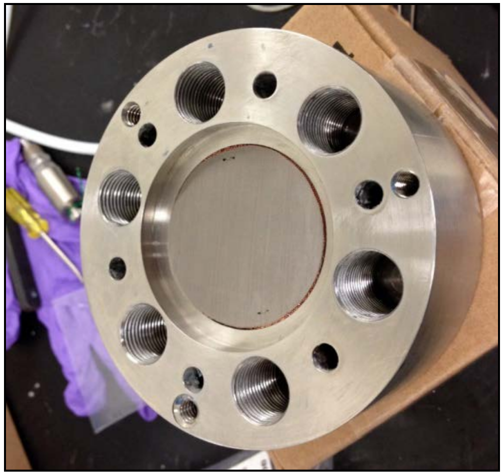
Progress – Devised robust frits for specimen support in vessel

- Polymer specimen requires porous, high-modulus support on the downstream and upstream sides
  - Pressure-induced flexure of the specimen could fatigue the polymer or alter the permeation measurements
- Quartz frits, which worked acceptably well for smaller diameter specimens or lower pressures, are crushed by the large force applied by the specimen
- Stacked metal mesh is an acceptable replacement for the quartz frit

Multiple discs of woven copper wire cloth (60 mesh) stacked and sewn together using 316 SS wire





Stacked metal mesh “frit” in vessel flange, with 316 SS disc (325 mesh) facing specimen

A porous disc fashioned from carbon fiber reinforcement similar to that in the tank shell might be an ideal frit.

Plan for remainder of FY 2013

- The four highest-priority durability measurements are for the following liner materials:
  1. **Injection-molded HDPE**
  2. **Rotomolded HDPE**
  3. **Extruded PA-6**
  4. **Blow-molded PET**
- The two medium-priority measurements are for the following liner materials:
  5. Extruded PA-6, with carbon black additive
  6. Injection molded HDPE with nano clay
- Materials 1, 2, 3 and 5 are currently in use as liners in Type 4 tanks. Polymers 4 and 6 are being considered for use as liners.

Plan for remainder of FY 2013

- **To complete durability measurements on the four highest-priority polymers by the end of FY 2013, we have implemented an abbreviated temperature cycling-permeation measurement protocol to provide a quick screening evaluation**:
  - Maintain the total number of temperature cycles (1,500)
  - Perform temperature cycling at 700 bar hydrogen pressurization
  - Measure *P* at -40, -10, 30 and 85◦C before the cycling begins and at the completion of 500 and 1,500 cycles (beginning, midpoint and end)
  - Model observed changes in *P* and predict leakage behavior of tank liner over 1,500 cycles

Proposed Future Work

- Continue temperature cycling and permeation measurements on medium-priority polymers
- Extend temperature cycling beyond 1,500 cycles for select polymers
- Repeat temperature cycling at 350 bar and compare results to those at 700 bar to assess effects of higher pressure
- Perform small number of temperature cycling and permeation measurements using H_2 containing concentrations of likely contaminants
- Continue development of test methodology for temperature cycling in sectioned storage tank
  - Obtain a better understanding of how liners function when situated in proximity to the composite reinforcement
  - If absorption of H_2 in the liner produces volumetric expansion of the liner or if the volume between liner and reinforcement layers becomes pressurized, this could pose a delamination concern
  - Provide a direct measurement of tank liner leakage as a function of cycle life

Project Summary

Relevance: Verify abilities of present and future polymer liners in Type 4 pressurized storage tanks to maintain leakage specification during the anticipated cycle life of the storage systems

Approach: Use extreme temperature cycling of polymer specimens, combined with high-pressure hydrogen permeation measurements, to predict tank liner leak rates as a function of the number of fill or temperature cycles

Technical Accomplishments/Progress: Developed test methodology; demonstrated that temperature cycling can produce microscopic changes in polymer structure (changes in permeation activation energy and pore size)

Technology Transfer/Collaborations: Manufacturers of high-pressure composite tanks, polymer manufacturers, and polymer and tank liner experts

Proposed Future Research: Use temperature cycling systems to test durability of polymers proposed for HFCT applications; perform lifecycle testing of liner material bonded to the composite matrix layer for *in toto* evaluation of the tank liner durability

Technical Backup Slides

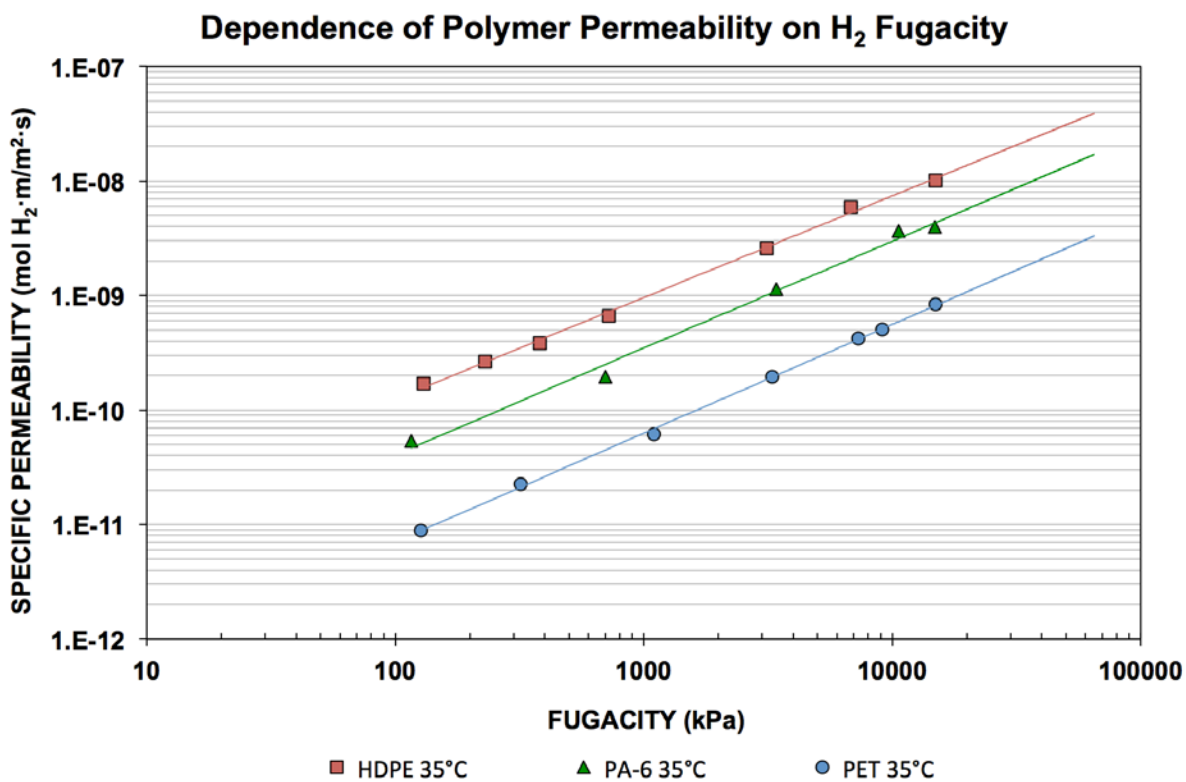
Accomplishments – Observed that H_2 permeation in polymers is not linearly dependent on fugacity

H_2 does not dissociate prior to dissolution and transport in polymers, thus the concentration of H_2 dissolved in the polymer should be linearly proportional to the H_2 fugacity, and $P = D \cdot S$ where D is the diffusion constant and S is the solubility

- We observed a *slight* deviation from a linear dependence of P_{sp} on fugacities from 1 to 140 bar in all polymers tested
- The deviation from linearity follows the modulus E:

	$P \sim f^{\alpha(E)}$	E (MPa)
HDPE:	$\alpha=0.89$, $\sigma=0.02$	1000
PA-6:	$\alpha=0.95$, $\sigma=0.05$	2400
PET:	$\alpha=0.95$, $\sigma=0.01$	3100

- The lower the modulus, the more compressible the polymer, and the less linear the dependence of P_{sp} on fugacity.



Accomplishments – Observed that H_2 permeation in polymers is not linearly dependent on fugacity

- Additional evidence that P_{sp} is dependent on polymer compressibility: The dependence of the permeability of PA-6 on fugacity becomes more linear with decreasing temperature. The polymer becomes less compressible as the temperature decreases and modulus increases.