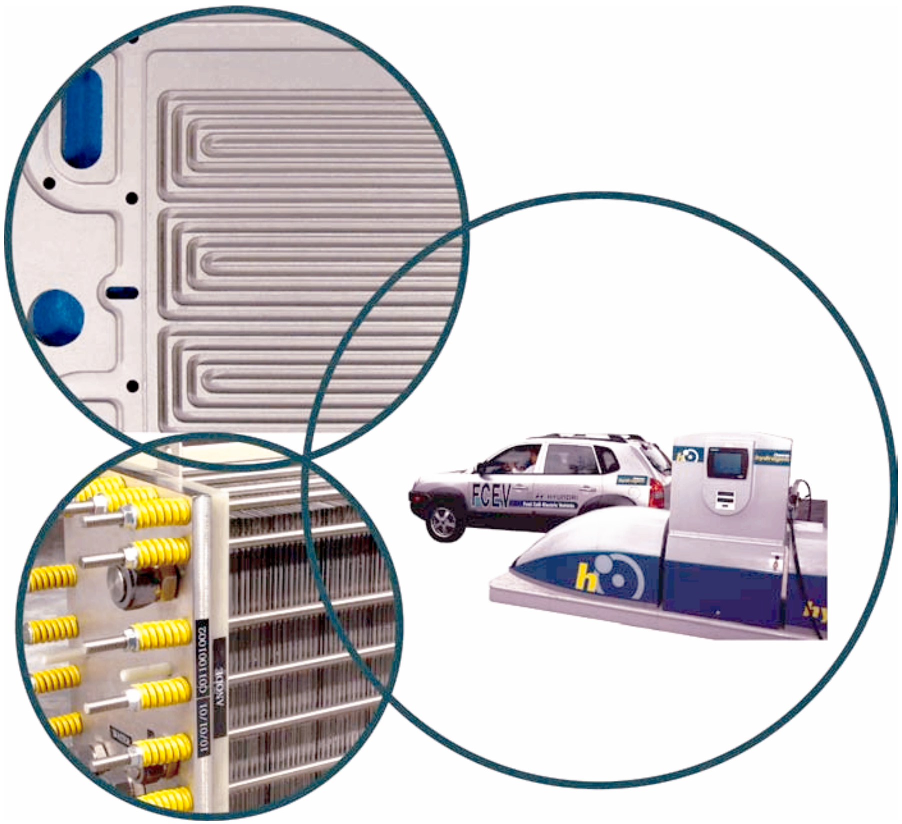
Lifecycle Verification of Polymeric Storage Liners



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Annual Merit Review
Washington, DC
May 11, 2011

Project ID #: ST053

OAK RIDGE National Laboratory

Overview

Timeline

- Start: June 2008
- Finish: Project continuation & direction determined annually by DOE

Budget

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

Partners & Collaborators

- Lincoln Composites
- Quantum Technologies

Technical Barrier

- Project addresses following barrier for on-board storage systems:
  - D. Durability/Operability

Technical Targets

- Project addresses the following technical targets for on-board storage systems:
  - Cycle life variation:

    FY 2010: 90%; FY 2015: 99%
  - Environmental health & safety:

    Meets or exceeds applicable permeation and leakage standards

    Loss of useable H_2 (in g/h/kg H_2) FY 2010: 0.1; FY 2015: 0.05

Relevance – Objective and Milestones

<u>Project goal:</u> Perform durability qualification measurements on polymeric tank liner specimens and assess ability of liner materials to maintain required hydrogen barrier performance

Month-Year	Milestone or Go/No-Go Decision
April 2011	Milestone: Thermal cycling and permeation measurements in Quantum Technologies liner material at 430 bar completed, trend in permeability change determined, and extent of microcracking assessed. (90% complete)
July 2011	Milestone: Hydrogen solubility measurements in liner materials completed, hydrogen uptake quantified, and possible effects of hydrogen-induced swelling in tank liner evaluated. (15% complete)
September 2011	Milestone: Go/No-Go decision on acceptability of existing liner materials (25% complete)

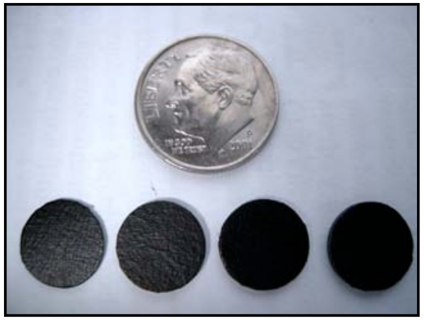
Relevance – Technical targets for on-board storage

- The Technical Plan for Storage* has durability targets for on-board storage for LDVs
  - Durability target for compressed storage tanks:
    - Lifecycle: 1500 fill cycles (cycle = 1/4 tank ↔ full tank)
    - Permeation and leakage of tank must meet applicable standards, *e.g.* 75 Ncc H_2/min
    - Cycle life variation for permeation and leakage must not exceed 99% of mean with a 90% confidence interval
- SAE J2579 does not specifically address lifecycle testing of the tank liner
- Project objective is to verify tank liner meets permeation and leakage standards throughout tank lifecycle

*Fuel Cell Technologies Program MYRDD Plan, Table 3.3.2, April 2009.

Technical Highlights – Temperature cycling produces structural changes

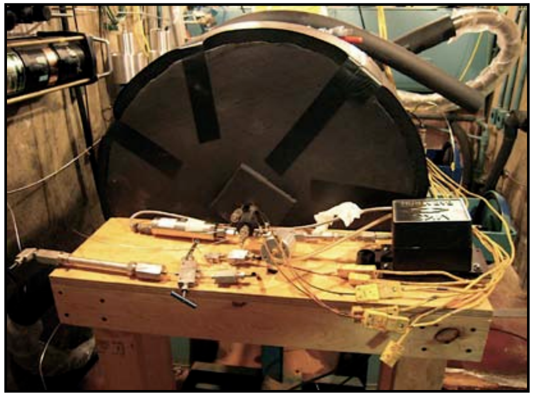
- Permeation measurements on specimen of Lincoln Composites Type IV tank liner (HDPE) show progressive change in the slope and pre-exponential factor of the permeation curves as a function of increasing temperature cycles
- Characterization of liner using neutron scattering and electron microscopy (SANS, USANS, SEM/BSE) show significant structural changes



1-cm dia. x 1-mm thick tank liner specimens

Technical Approach – Test protocol

- Verify durability of polymer liners in high-pressure storage tanks
  - Subject polymer specimens to extreme-temperature cycling while specimens are differentially pressurized with hydrogen
  - Measure hydrogen permeation at prescribed intervals to assess the ability of the liner materials to maintain the required hydrogen barrier capability.
  - Use test protocol derived from SAE J2579, *Technical Information Report for Fuel Cell and Other Hydrogen Vehicles* (Jan 2008)



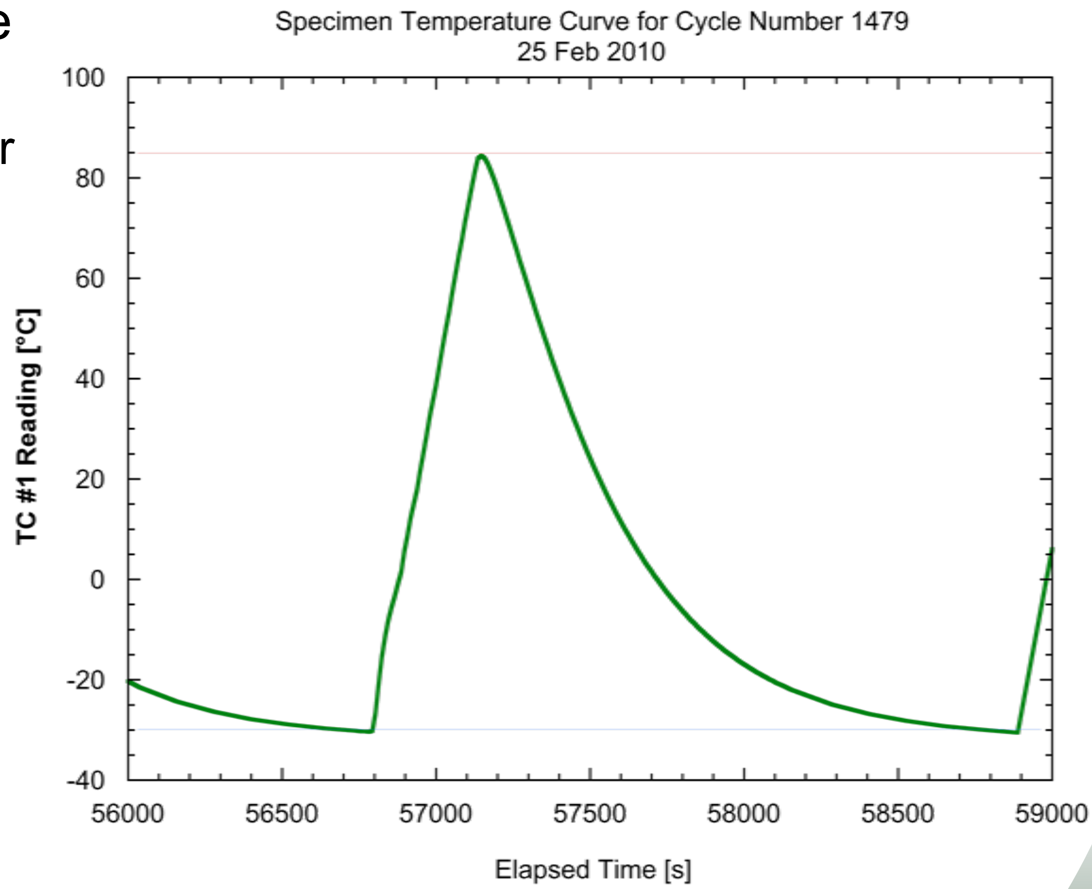
High-pressure temperature cycling test vessel

Technical Approach – Test Protocol

- From SAE J2579 § 5.2.2 (January 2008)
  - 5500 temperature cycles: -30 to 85°C
    - Upper temperature for specimen (85°C) is limited by glass transition temperature for polymer; lower temperature is determined by limitations of high-pressure seals in apparatus
    - Cycle consists of 5.75 minute heating interval (+20°C/minute), followed by 28 minute cooling interval (~2 cycles per hour)
  - Upstream hydrogen pressures: 430 and 860 bar (6,250 and 12,500 psia)
- Measure permeation rates at -30, 25, 60 and 85°C at completion of every 250 cycles (250-1500 cycles) and 500 cycles (2000-5500 cycles)

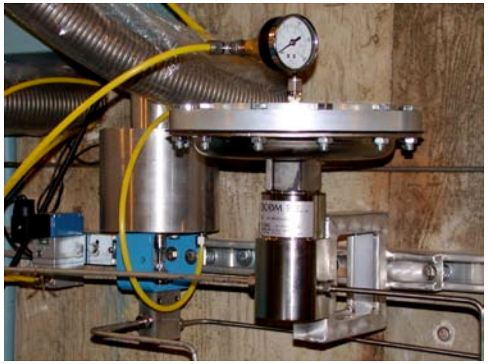
Technical Approach – Temperature cycle of rapid heating with slow cooling

- Temperature cycling profile
  - 5.75 min heating interval corresponds to a 20°C per min heating rate
  - 27.6 min cooling interval determined by thermal mass of specimen holder
  - Allows approximately 43 cycles per day or 302 cycles per week



Technical Approach – Temperature cycling with high differential pressure

- Constant pressure differential maintained using computer-controlled accumulator/
  regulator system
  - High upstream pressure maintained during temperature cycling using computer-controlled high-pressure regulator fed from high-pressure large-volume accumulators
  - Downstream pressure is maintained at a value below atmospheric pressure during cycling, allowed to rise to measure
    permeation rate



High pressure hydrogen regulator

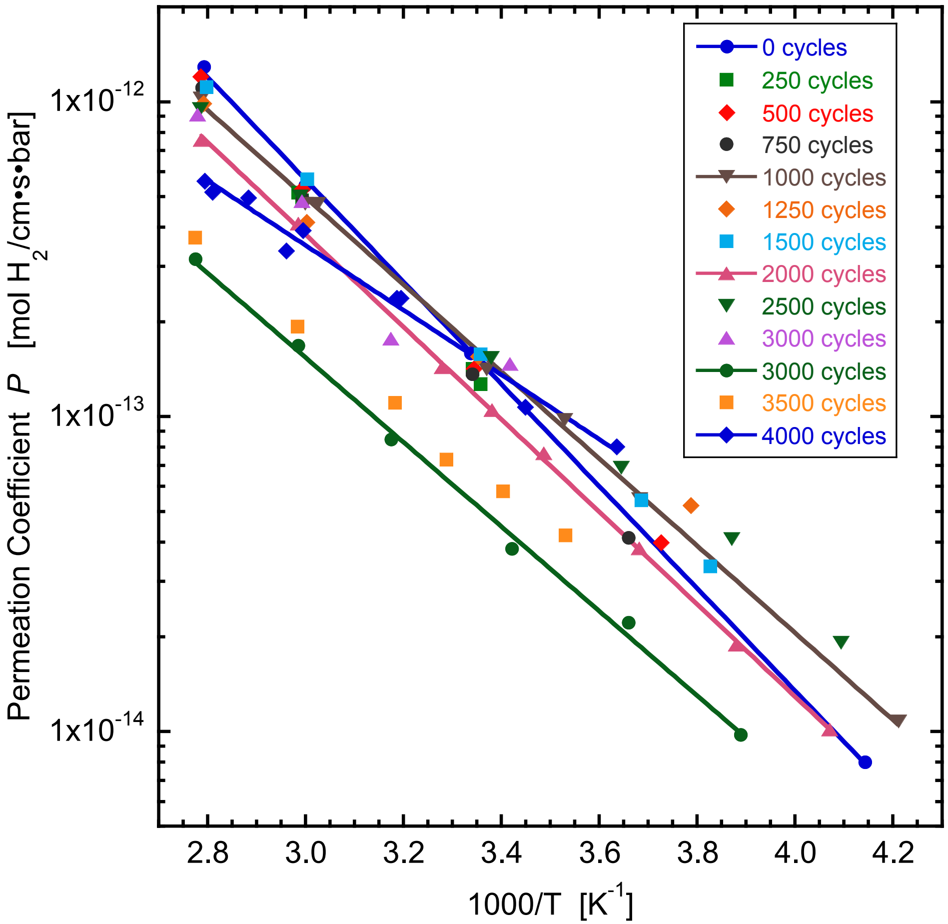
High pressure hydrogen accumulators

Technical Progress – Completed 4000 temperature cycles

- Completed permeation measurements* during 4000 temperature cycles
  - Temperature dependence of permeation coefficient is described by Arrhenius relationship

    $$P = P_0 \exp(-E_A/RT)$$

  - Measurement intervals: 0, 250, 500, 750, 1000, 1250, 1500, 2000, 2500, 3000, 3500, 4000 cycles
  - Decreasing slope with cycles indicates changes occurring in P_0 and E_A

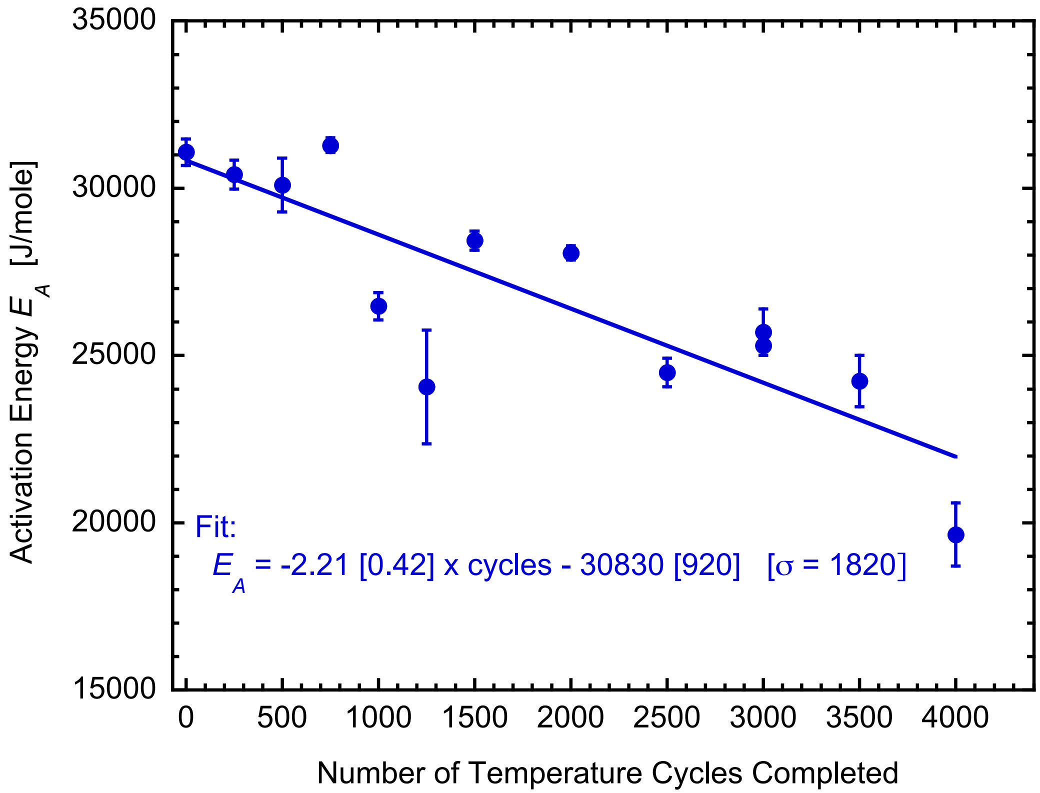


Permeation coefficients *P* for hydrogen in polymer specimen, measured at 430 bar.

*Measurements conform to ASTM D1434, *Determining Gas Permeability Characteristics of Plastic Film and Sheeting* (2003).

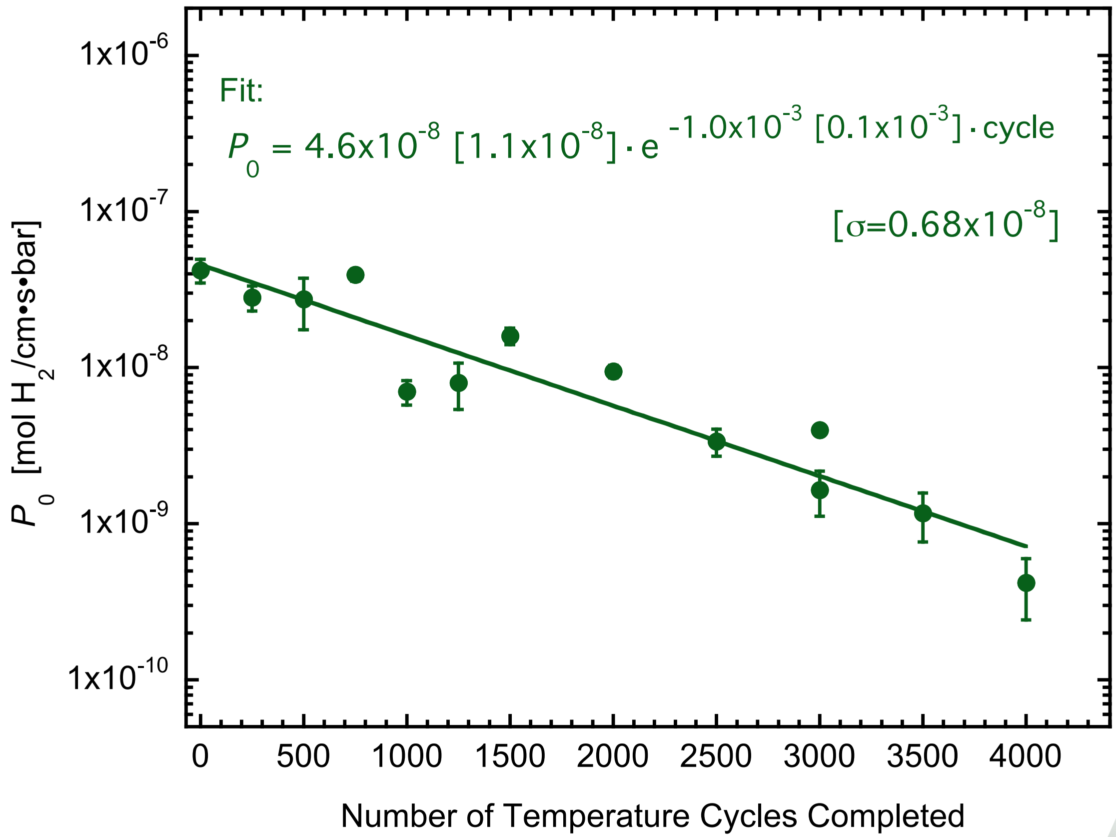
Technical Progress – Changes observed in activation energy of permeation process

- Analysis of activation energy E_A
  - Changes in E_A as specimen is subjected to repeated cycling could indicate polymer is undergoing microscopic changes in polymer matrix
  - Measurements show that E_A is decreasing with increasing number of temperature cycles (slope in plot of E_A *vs* cycle count is 5 standard deviations from zero)



Technical Progress – Changes observed in pre-exponential factor

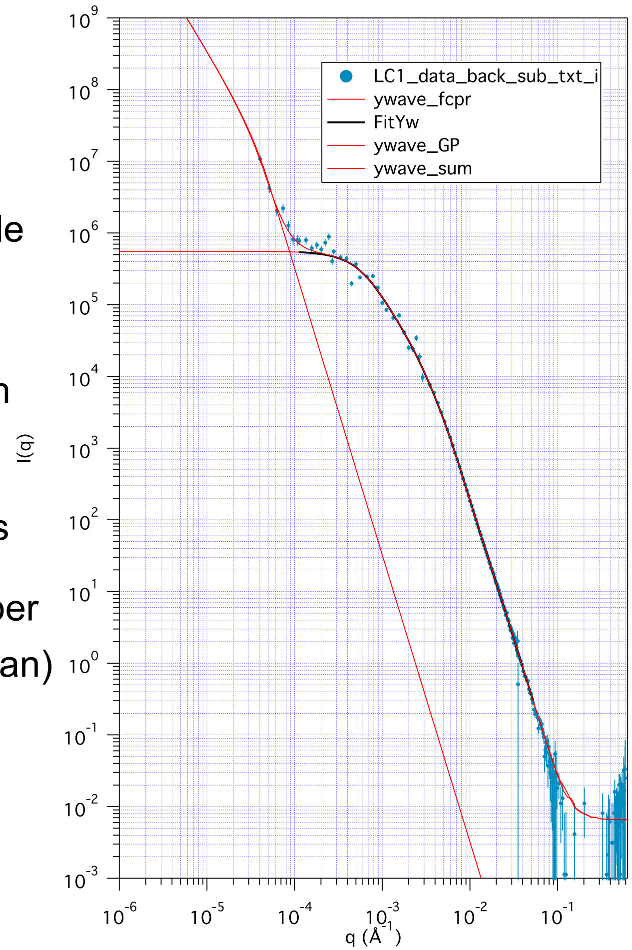
- Analysis of pre-exponential factor P_0
  - Changes in P_0 as specimen is subjected to repeated cycling could also indicate polymer is undergoing microscopic changes in polymer matrix
  - Measurements show that P_0 is decreasing with increasing number of temperature cycles, (slope in plot of log P_0 *vs* cycle count is 4 standard deviations from zero)

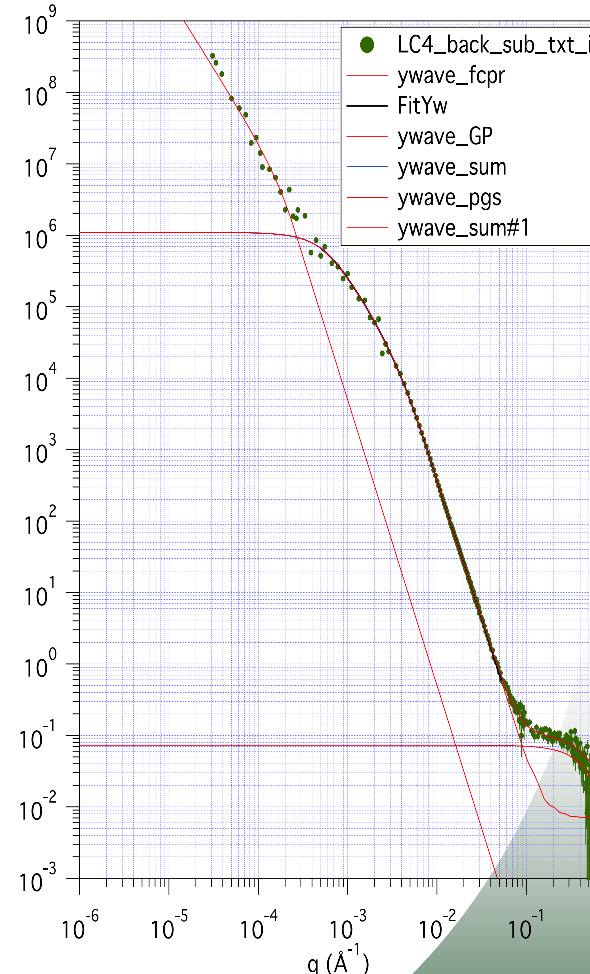


Technical Progress – Neutron scattering measurements

Small- and Ultra Small-Angle Neutron Scattering (SANS and USANS)

- Measurements performed at NIST/NCNR in Feb 2011
- Looked for structural changes in polymer on the scale ~1 nm to ~30 μm
- Samples analyzed: 1) HDPE sample before temp cycling (plot on left), 2) sample after only a few temp cycles, 3) sample after 600 cycles, 4) sample after 4000 cycles (plot on right)
- Central section modeled as flexible cylinder with a polydispersed radius model designed for polymers* increased intensity with cycle number
- High-Q fit to polydispersed (Gaussian) sphere model – only appears after hydrogen exposure
- Low-Q fit to Guinier-Porod model – hydrogen exposure changes slope from -4 (Porod) to -2 (Guinier for plates or laminae). Intensity increases, Guinier-Porod transition shifts with increasing cycle number



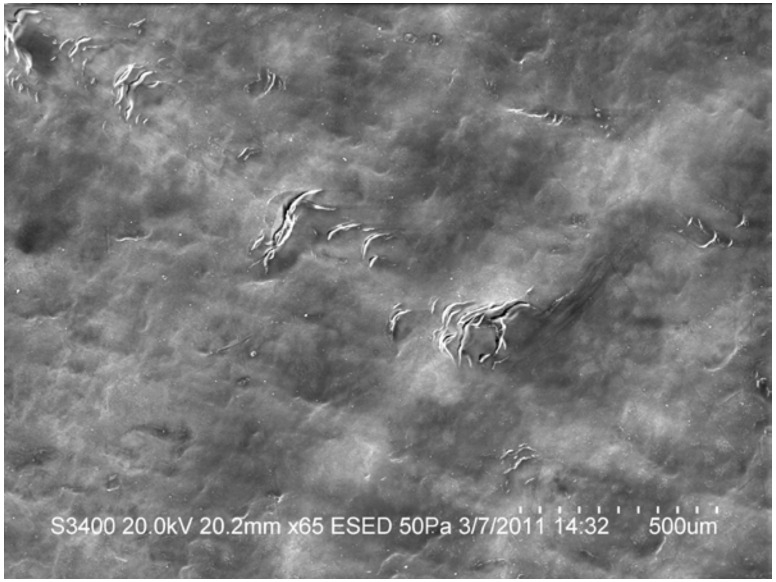


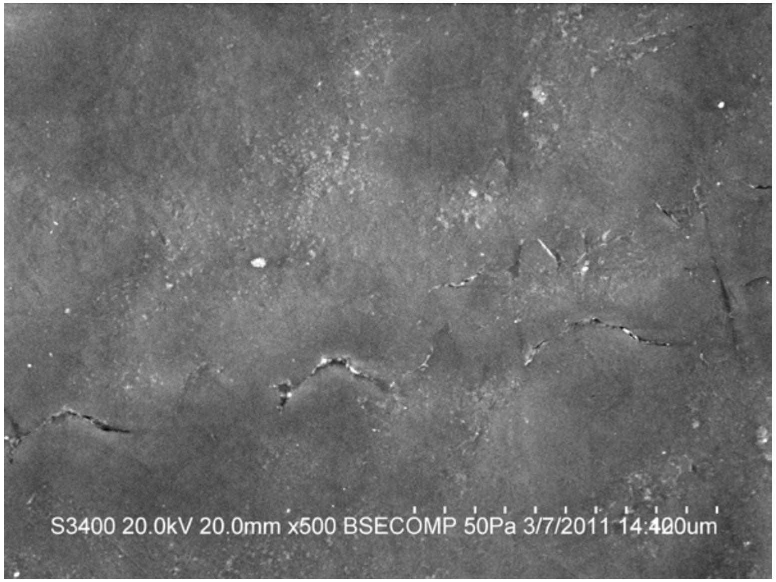
*See B. Hammouda, *The SANS Toolbox*, NIST Center for Neutron Research, available at http://www.ncnr.nist.gov/staff/hammouda/the_SANS_toolbox.pdf

Technical Progress – Electron Microscopy of Specimens

Scanning Electron Microscopy

- The presence of the low-Q scattering in the (U)SANS data shows that there are large-scale (> ~30 mm) scattering features in these samples that change significantly with long-term high-pressure hydrogen exposure and increasing number of temperature cycles
- SEM analysis was used to observe these features (completed to date only for the starting material as the experimental materials have not yet been released/returned from NIST/NCNR)
- Images below show secondary (left) and backscattered (right) electron images of the Lincoln Composites HDPE before cycling. Small fractures and other irregularities are visible that may be the source of this scattering. Additional work and complementary TEM imaging are necessary to resolve the origin of these features and determine their relationship to changes in permeability





Collaborations

- **Lincoln Composites – tank liner specimens**
- **Quantum Technologies – tank liner specimens**

Future Work

- FY 2011
  - Complete post-cycling analysis of Lincoln Composites specimen cycled at 430 bar (6,260 psia)
  - Complete temperature cycling of Lincoln Composites specimen at 860 bar (12,500 psia) pressurization
  - Complete first 1,500 temperature cycles on Quantum Technologies specimen at 430 bar pressurization using new apparatus
  - Begin hydrogen solubility measurements in HDPE specimens
- FY 2012
  - Complete temperature cycling of Quantum Technologies specimen at 860 bar pressurization
  - Complete temperature cycle testing of an alternative liner material (PA-6) and compare to HDPE liner materials
  - Report results of all lifecycle verification measurements and report assessments

Project Summary

Relevance:	Durability of polymeric tank liners over the performance lifetime of high-pressure storage systems must be verified and validated
Approach:	Use relevant portion of SAE J2579 to develop and carry out durability test cycling measurements
Progress:	Measurement of permeation coefficients through 2000 cycles suggests slight changes in polymer microstructure, but no indication that liner permeability has been adversely affected
Collaborations:	Lincoln Composites, Quantum Technologies, Ticona
Future:	Long-term measurements of multiple liners at 430 and 860 bar, possible measurements of alternative liner materials, measurements of hydrogen solubilities in tank liner polymers