New Materials for Hydrogen Pipelines

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Hydrogen Pipeline Working Group Meeting
August 30-31, 2005
Augusta, Georgia

Overview – Barriers and Technical Targets

- **Barriers to Hydrogen Delivery**
  - Existing steel pipelines are subject to hydrogen embrittlement and are inadequate for widespread H_2 distribution.
  - Current joining technology (welding) for steel pipelines is major cost factor and can exacerbate hydrogen embrittlement issues.
  - New H_2 pipelines will require large capital investments for materials, installation, and right-of-way costs.
  - H_2 leakage and permeation pose significant challenges for designing pipeline equipment, materials, seals, valves and fittings.
  - H_2 delivery infrastructure will rely heavily on sensors and robust designs and engineering.

Alternatives to metallic pipelines - pipelines constructed entirely from polymeric composites and engineered plastics – could enable reductions in capital costs and provide safer, more reliable H_2 delivery.

Overview – Technical Barriers and Targets

Category	2003 Status	2005	2010	2015
Pipelines: Transmission				
Total Capital Cost ($M/mile)	$1.20	$1.20	$1.00	$0.80
Pipelines: Distribution				
Total Capital Cost ($M/mile)	$0.30	$0.30	$0.25	$0.20
Pipelines: Transmission and Distribution				
Reliability (relative to H_2 embrittlement concerns and integrity)	Undefined	Undefined	Understood	High (Metrics TBD)
H_2 Leakage	Undefined	Undefined	<2%	<0.5%

From Table 3.2.2, Hydrogen Delivery Targets, in *DOE Hydrogen, Fuel Cells & Infrastructure Technologies Program: Multi-year research, development and demonstration plan*, Jan. 21, 2005.

Objectives

- **Investigate the use of fiber-reinforced polymer (FRP) pipeline technology for transmission and distribution of hydrogen, to achieve reduced installation costs, improved reliability and safer operation of hydrogen pipelines.**
- **Develop polymeric nanocomposites with dramatically reduced hydrogen permeance for use as the barrier/liner in non-metallic hydrogen pipelines.**

Advantages of Continuous FRP Piping

- Anisotropic characteristics of FRP piping provide extraordinary burst and collapse pressure ratings, increased tensile and compressive strengths, and increased load carrying capacities.
- No welding and minimal joining - Many miles of continuous pipeline can be emplaced as a seamless monolith.
- Emplacement requirements should be dramatically less than those for metal pipe, enabling the pipe to be installed in areas where right-of-way restrictions are severe.
- Corrosion resistant and damage tolerant.
- Structurally integrated sensors provide real-time structural health monitoring and could reduce need for pigging.
- Meets or exceeds published and consensus standards for pipeline in oil and gas applications.

Approach

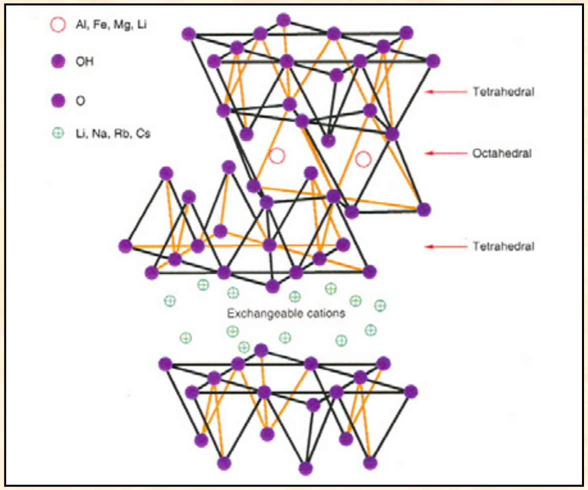
- **Fiber-reinforced polymer (FRP) hydrogen pipeline**
  – Assess applicability of FRP technology for hydrogen transmission and distribution pipelines
  – Assess methods for achieving technical targets for hydrogen delivery using FRP pipelines
  – Identify potential manufacturing options and joining/repair techniques
  – Determine requirements for making technology economically and practically feasible

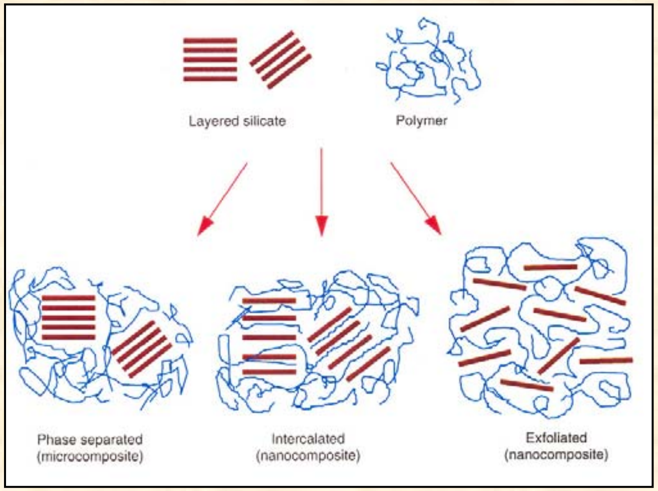
Pictures provided courtesy of FiberSpar Corp.

Picture provided courtesy of Ameron International.

Approach

- **Nanostructured plastics with reduced hydrogen permeance**
  - Synthesize polymer-layered silicates using organo-modified montmorillonite (clay) in polyethylene terephthalate (PET)
  - Evaluate the hydrogen permeability and mechanical properties of sample coupons of modified PET
  - Optimize permeance of modified PET by adjusting organo-modifier, clay loading, and extrusion conditions.





Overview – Budget

Task	FY 2005
1. Investigate feasibility of using fiber-reinforced polymer pipeline for H_2 transmission and distribution	$75K
2. Develop nanostructured plastic for use as non-permeable liner in H_2 pipelines	$75K
Total	**$150K**

Interactions and Collaborations

- **Existing**
  - Hydrogen Pipeline Working Group
  - University of Tennessee Department of Chemistry - synthesis of plastics with polymer-layered silicates
- **Pending**
  - Fiber-reinforced polymer pipelines: U.S. manufacturers of composite piping and storage tanks
  - Pipeline infrastructure: Natural gas industries
  - Pipeline materials qualification: Savannah River National Laboratory
  - Others

Technical Accomplishments

- **FRP Piping Feasibility – Capital Cost Estimate**
  - Average hydrogen demand of 0.5 kg H_2 per day per capita was calculated from technical targets and existing transportation data. However, demand varies diurnally and seasonally, so peak demand of 1.5 times average demand was used as basis for the cost estimate.
  - Assume hydrogen generation plant is 200 miles from the population it serves.
  - Spoolable composite piping is available in sizes up to four-inch ID and with pressure ratings up to 3000 psi. Larger composite pipes were also considered in this analysis.
  - Assume H_2 enters pipeline at 1000 psi pressure and the allowable pressure drop is 300 psi.
  - Estimate pipeline sizes required to serve populations of 100,000, 1,000,000 and 10,000,000 people.

Technical Accomplishments

- **FRP Piping Feasibility – Capital Cost Estimate (continued)**

	Pipeline Requirements for H_2 Delivery Assuming 1,000 psi Source Pressure and 300 psi Pressure Drop				
Population Served	**Peak H_2 Demand (kg/h)**	**4-inch Pipelines Req'd**	**8-inch Pipelines Req'd**	**12-inch Pipelines Req'd**	**I.D. for Single Pipeline (inches)**
100,000	3,000	5	1	(1)	8
1,000,000	30,000	50	9	3	18
10,000,000	300,000	500	90	30	44

Technical Accomplishments

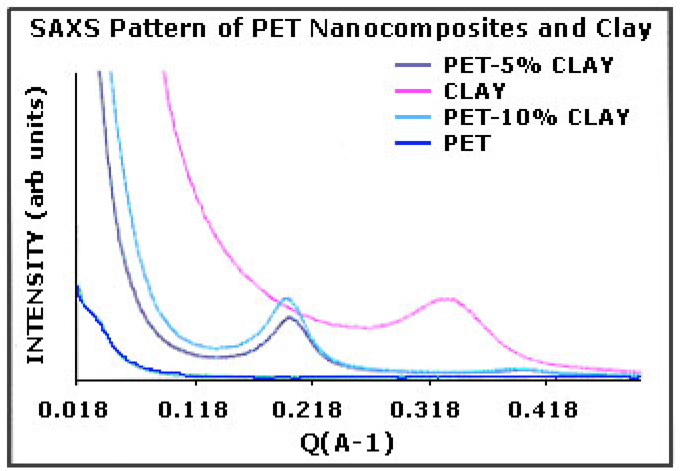
- **FRP Piping Feasibility – Capital Cost Estimate (continued)**
  - Current capital cost (materials and installation) for 4-inch ID, 1000 PSI-rated FRP piping is $50K to $100K per mile.
  - Transmitting H_2 to a population of 100,000 would require five 4-inch ID pipelines, at an approximate capital cost of $250K to $500K per mile, not including right-of-way costs.
  - This estimate is below the DOE 2015 target for hydrogen delivery ($800K per mile).
  - However, current fiber-reinforced piping needs liner with acceptably low hydrogen permeation and needs qualification for high-pressure H_2 service.

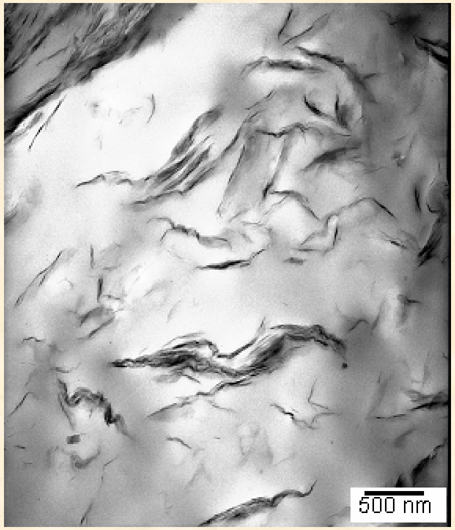
Technical Accomplishments

- **Preparation and evaluation of PET/clay nanocomposites**
  - Synthesized nanocomposites by solution mixing PET and organo-modified clay in phenol/chloroform solvent
  - Prepared PET nanocomposites with clay contents of 5 and 10 wt%
  - Modified PET films prepared for analysis and testing by pressing dried mixtures of PET/clay into thin membranes
  - Evaluated nanostructure of films using SAXS and TEM
  - Evaluated hydrogen permeability using ORNL hydrogen service IHPV test facility

Technical Accomplishments

- **Small-angle x-ray scattering (SAXS)**
  - Intercalation of PET chains increases interlayer spacing, shifting peak to lower Q values
  - Exfoliation of PET/clay would be evidenced by broadening of peak

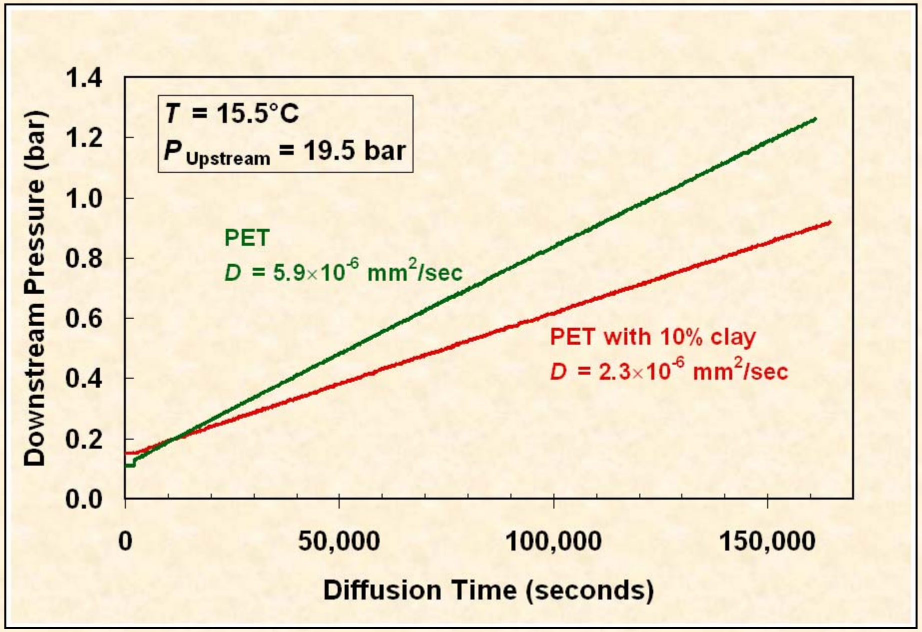


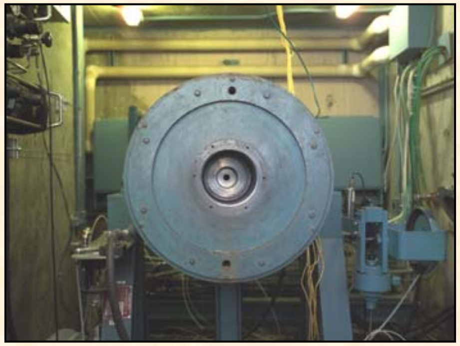


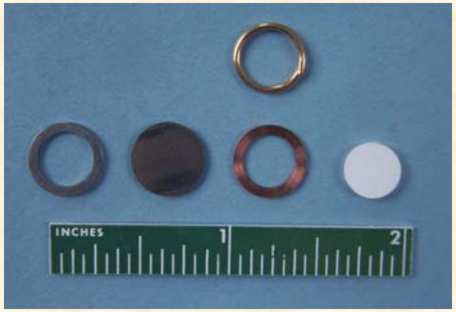
- **Transmission electron microscopy (TEM)**
  - Images of PET with 5% (left) and 10% (right) clay contents
  - Clay appears as dark lines
  - Most clay occurs as intercalated clusters with only partial exfoliation

Technical Accomplishments

- H_2 permeation measurements in ORNL IHPV
  - Initial modified PET sample exhibited 60% decrease in diffusion rate coefficient







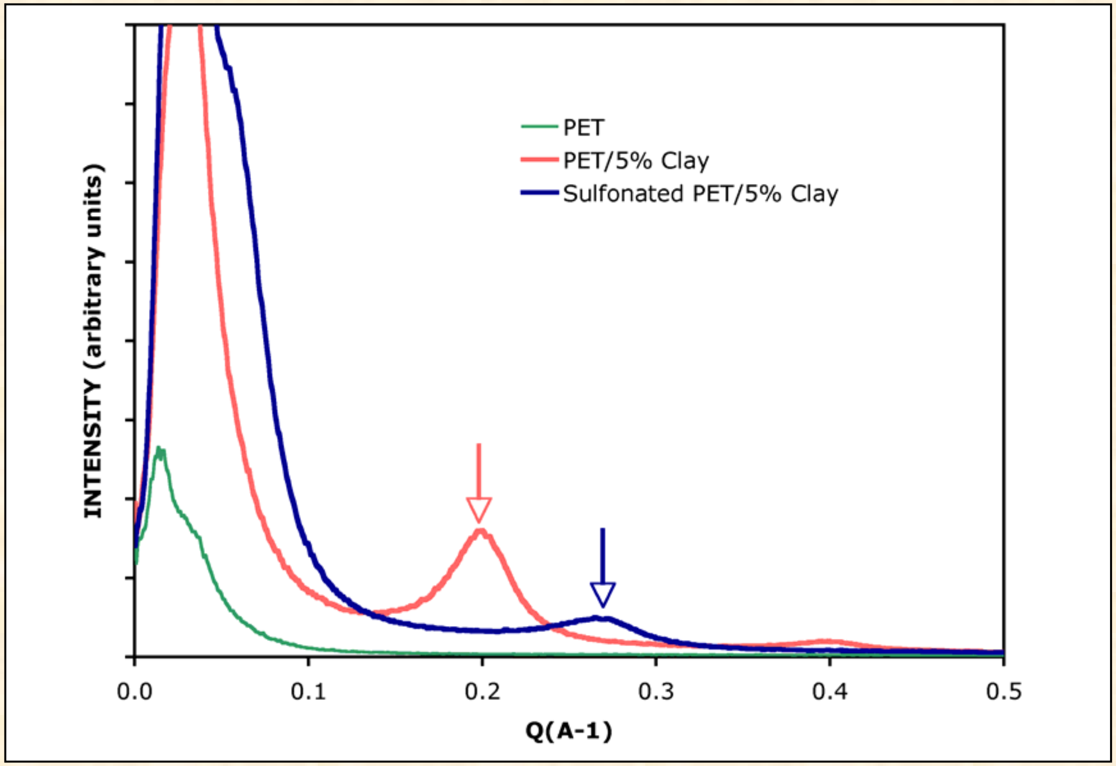
Technical Accomplishments

- **Preparation and evaluation of sulfonated PET/clay nanocomposites**
  - Second formulation of PLS nanocomposites involved partial sulfonation of PET to obtain a higher degree of exfoliation.
  - A white solid powder of PET with 3% sulfonation was produced.
  - Nanocomposites were prepared in sulfonated PET (s-PET) by solution mixing and films were pressed at high temperature and pressure.
  - PET/clay samples with clay contents of 5 and 10 wt % were prepared for analysis and testing by pressing dried mixtures of PET/clay into thin membranes
  - Evaluated clay dispersion in films using SAXS
  - Evaluated hydrogen permeability using ORNL hydrogen service IHPV test facility

Technical Accomplishments

- **Evaluation of sulfonated PET/clay nanocomposites**

SAXS profiles of neat PET, PET/5% clay and s-PET/5% clay.



Technical Accomplishments

- **Summary of permeation measurements to date**

Sample	***T* (°C)**	***D* ($\times 10^{-4}$ cm^2/s)**
PET	15	5.9
PET/10% clay	16	2.3
s-PET	22	18.2
s-PET/5% clay	23	12.2
Kynar (PVF)	24	Similar to PET

Future Work – Milestones

- **FY 2005**
  - On schedule to complete milestones
    - May 2005 - PET-based polymer-layered silicate composite barrier materials prepared and ready for permeability testing.
    - Sep 2005 - Report on FRP pipeline feasibility and recommendations to be completed.
    - Sep 2005 - Assessment of hydrogen permeability in barrier material coupons to be completed.
- **For FY 2006**
  - Recommendations for sensor integration, manufacturing and joining technologies
  - Further optimization of nanostructured plastic liner
  - Bench-scale tests of integrated nanostructured plastic liner and FRP pipe