New Materials for Hydrogen Pipelines

Barton Smith, Barbara Frame, Cliff Eberle, James Blencoe, Larry Anovitz and Tim Armstrong Oak Ridge National Laboratory

> Jimmy Mays University of Tennessee, Knoxville

2005 DOE Hydrogen Program Annual Review

May 25, 2005

Poster Presentation PDP 51

This presentation does not contain proprietary or confidential information.



Overview – Barriers and Technical Targets

Barriers to Hydrogen Delivery

- Existing steel pipelines are subject to hydrogen embrittlement and are inadequate for widespread H₂ distribution.
- Current joining technology (welding) for steel pipelines is major cost factor and can exacerbate hydrogen embrittlement issues.
- New H₂ pipelines will require large capital investments for materials, installation, and right-of-way costs.
- H₂ leakage and permeation pose significant challenges for designing pipeline equipment, materials, seals, valves and fittings.
- H₂ 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 – Barriers and Technical Targets

- Hydrogen Delivery Technical Targets (2015)
 - Total capital cost of transmission pipelines: \$800K/mile
 - Total capital cost of distribution pipelines: \$200K/mile
 - High pipeline reliability: equivalent to today's natural gas pipeline infrastructure
 - Loss due to leakage and permeation: < 0.5% of H₂ put through pipeline





- Investigate feasibility of using fiber-reinforced polymer (FRP) pipeline for transmission and distribution of hydrogen to provide reduced installation costs, improved reliability, and safe operation.
- Develop nanostructured plastic with dramatically reduced hydrogen permeance for use as the barrier/liner in nonmetallic H₂ pipelines.



Advantages of Continuous FRP Piping

- Anisotropic characteristics of FRP piping provide extraordinary burst and collapse pressure ratings, increased tensile and compression strengths, and increased load carrying capacities.
- No welding.
- Nearly jointless many miles of continuous pipe can be installed as a seamless monolith.
- Placement requirements could be dramatically less than those for metal pipe, enabling the pipe to be installed in areas where rightof-way restrictions are severe.
- Corrosion resistant and damage tolerant.
- Structurally integrated sensors will provide real-time structural health monitoring and could reduce need for "pigging".





• Fiber-reinforced polymer (FRP) pipeline for H₂

- Identify performance targets for H₂ pipelines as they relate to FRP technology.
- Identity potential manufacturing options and joining/repair techniques.
- Determine what is required to make the technology economically feasible.



Picture provided courtesy of FiberSpar.



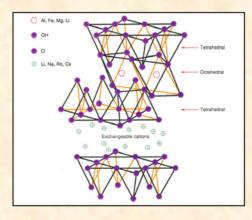
Picture provided courtesy of Ameron International.

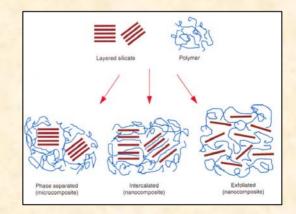




Nanostructured plastic with reduced H₂ permeance

- Synthesize nanocomposites in polyethylene terephthalate (PET) using layered organo-modified nanostructured montmorillonite (clay).
- Evaluate hydrogen permeability and mechanical properties of sample coupons of modified PET.
- Optimize permeance of modified PET by adjusting organo-modifier, montmorillonite loading, and extrusion conditions.







Overview – Project Timeline

Task 1: Investigate feasibility of FRP pipeline for H₂ transmission and distribution

FY 2005	FY 2006	FY 2007	
1 2 3	4 5	6	

- New start project began January 2005
- Subtasks
 - FY 2005
 - 1 Identify pipeline requirements
 - 2 Perform point design
 - 3 Identify advantages and challenges of manufacturing methods
 - 4 Assess feasibility of technology
 - FY 2006
 - 5 Perform bench-scale tests of integrated modified-PET liner and FRP pipe
 - 6 Develop sensor integration, manufacturing, joining technologies
 - FY 2007
 - 7 Demonstrate larger scale pipe with industry
 - 8 Recommend best manufacturing and placement methods



Overview – Project Timeline

Task 2: Develop nanostructured plastic barrier material

FY 2005	FY 2006	FY 2007	
1 2 3	4 5	6	

- New start project began January 2005
- Subtasks
 - FY 2005
 - 1 Synthesize clay nanocomposites in PET
 - 2 Extrude modified PET
 - 3 Test extruded samples for H2 permeability and mechanical properties
 - FY 2006
 - 4 Optimize non-permeability of modified PET
 - 5 Extrude liner for bench scale tests of FRP pipe
 - FY 2007
 - 6 Commercialize technology



Overview – Budget

Task	FY 2005	
1. Investigate feasibility of using fiber- reinforced polymer pipeline for H ₂ transmission and distribution	\$80K	
2. Develop nanostructured plastic for use as non-permeable liner in H ₂ pipelines	\$80K	
Total	\$160K	



Interactions and Collaborations

• Existing

- Hydrogen Pipeline Working Group
- Extrusion of modified PET: University of Tennessee Textiles and Nonwovens Development Center (TANDEC)

Pending

- Fiber-reinforced polymer piping: U.S. manufacturers of composite piping and storage tanks
- Pipeline infrastructure: Natural gas industries
- Pipeline materials qualification: Savannah River National Laboratory
- Others



Plastic non-permeable liner

- Synthesize nanocomposites in PET using layered organo-modified nanostructured clay (montmorillonite)
- Evaluate hydrogen permeability and mechanical properties of sample coupons of modified PET
- Optimize non-permeability by adjusting organo-modifier, montmorillonite loading, and extrusion conditions
- Fiber-reinforced polymer H₂ pipeline
 - Identify performance targets for H₂ pipeline transmission as they relate to FRP technology
 - Identity potential manufacturing options and joining/repair techniques
 - Report on requirements to make the technology economically feasible.



FRP Piping Feasibility Assessment

- Assume H_2 production plant 200 miles from population center.
- Estimate per capita H_2 demand of 0.5 kg/day for transportation use.

	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)	No. 4-inch Pipelines Req'd	No. 8-inch Pipelines Req'd	No. 12-inch Pipelines Req'd	I.D. for Single Pipeline (inches)	
100,000	3,000	5	1	n.a.	8	
1,000,000	30,000	50	9	3	18	
10,000,000	300,000	500	90	30	44	



• FRP Piping Feasibility Assessment (continued)

- Current capital cost (materials and installation) for 4-inch ID, 1000 PSI-rated fiber-reinforced polymer piping is \$50K to \$100K per mile.
- Transmitting H₂ to a population of 100,000 would require five 4-inch ID pipelines, at an approximate capital cost of \$250K to \$500K per mile.
- This estimate is well 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 H₂ service.



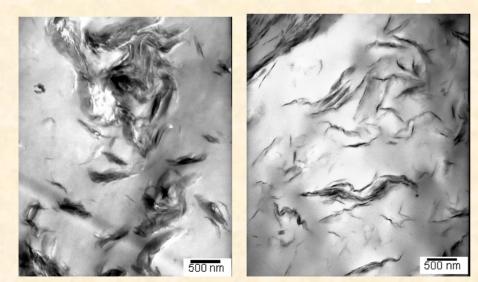
• Preparation and evaluation of PET/clay nanocomposites

- Synthesized nanocomposites by solution mixing PET and organomodified 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



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



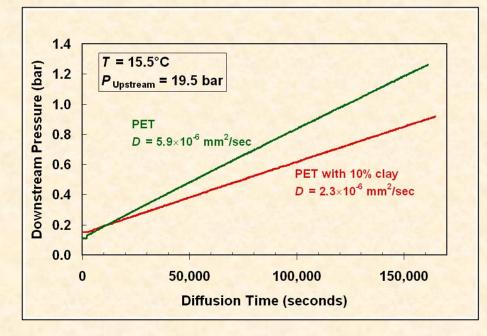
SAXS Pattern of PET Nanocomposites and Clay PET-5% CLAY CLAY PET-10% CLAY PET PET 0.018 0.118 0.218 0.318 0.418 Q(A-1)

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



- H₂ permeation measurements in ORNL IHPV
 - Initial modified PET sample exhibited 60% decrease in diffusion rate coefficient





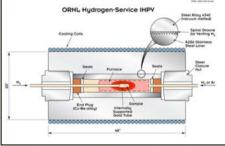


Photo and schematic of the internally heated high-pressure vessel.



Future Work – Milestones

Remainder of 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 completed.
 - Sep 2005 Assessment of hydrogen permeability in barrier material coupons completed and reported.

• For FY 2006

- Optimize synthesis of modified PET for minimal permeance.
- Extrude liner for bench scale tests of FRP pipe.
- Perform bench-scale tests of integrated modified-PET liner and FRP pipe.
- Develop sensor integration, manufacturing, joining technologies.



Hydrogen Safety

- The most significant hydrogen hazard associated with this project is the potential leakage of H₂ during permeation measurements in the IHPV (internally heated high-pressure vessel).
- All project activities, including the permeation measurements, are covered by a formal, integrated work control process for each practice/facility.
- Each work process is authorized on the basis of a Research Safety Summary (RSS) review by ES&H subject matter experts and approval by PI's and cognizant managers.
- The RSS is reviewed/revised annually or whenever a change in work is needed.
- Staff with approved training and experience are authorized through the RSS.

