

V.A.2 New Materials for Hydrogen Pipelines

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Start Date: January 2005

Projected End Date: Project continuation and direction determined annually by DOE

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 nanocomposite with dramatically reduced hydrogen permeance for use as the barrier/liner in non-metallic hydrogen pipelines.

Technical Barriers

This project addresses the following technical barriers from the Hydrogen Delivery section of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year Research, Development and Demonstration Plan:

- D. High Capital Cost and Hydrogen Embrittlement of Pipelines

Technical Targets

This purpose of this project is to develop fiber-reinforced polymer technology and engineered plastics for constructing high-pressure pipelines for hydrogen transmission and distribution. These materials can provide major cost reductions in pipeline construction compared to steel pipelines. The long-term objective is commercialization of non-metallic pipeline technology that attains the DOE hydrogen delivery performance and cost targets for 2015:

- Transmission pipeline total capital cost: \$800K per mile
- Distribution pipeline total capital cost: \$200K per mile
- Hydrogen delivery cost: <\$1.00/gge
- Transmission and delivery reliability: High, with metrics to be determined
- Hydrogen pipeline leakage: <0.5%

Approach

Fiber-Reinforced Polymer (FRP) 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 FRP technology economically and practically feasible

Polymeric nanocomposite with reduced H₂ permeance

- Synthesize polymer-layered silicates in polyethylene terephthalate (PET) using 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.

Accomplishments

- Assessed capital cost for FRP pipeline delivery of hydrogen from production center to population center, using existing commercially available pipeline technology, and found that cost estimate is below DOE 2015 target.
- Initial sample of modified PET (polymeric nanocomposite) with un-optimized loading of organo-modified clay additive showed 60% decrease in hydrogen permeability, compared to pure PET.

Future Directions

- Perform bench-scale tests of integrated sensor performance in short sections of FRP pipeline
- Evaluate feasibility of large-scale manufacturing operations
- Plan prototype manufacturing for a demonstration project
- Evaluate pipe joining technologies
- Extrude liner from modified PET (polymer-layered silicates [PLS] nanocomposite) and perform life-cycle tests
- Manufacture prototype FRP pipeline for hydrogen service
- Propose commercial demonstration of pipeline technology

Introduction

Gas pipelines are at present the lowest cost option for transmitting large quantities of hydrogen. However, the existing hydrogen pipeline technology cannot be extrapolated to achieve the cost and performance goals required for successful implementation of this distribution network.

Fiber-reinforced polymer (FRP) pipelines are emerging as a feasible alternative to steel pipelines with regard to performance and cost. An FRP pipeline is typically constructed including an inner non-permeable barrier tube that transports the fluid (pressurized gas or liquid), a protective layer over the barrier tube, an interface layer over the protective layer, multiple glass or carbon fiber composite layers, an outer pressure barrier layer, and an outer protective layer. An FRP pipeline is a composite structure in the purest engineering sense of the term, as each of the several components provides a distinct

function and the interaction between the components produces a structure with exceptional performance characteristics. The pipeline has improved burst and collapse pressure ratings, increased tensile strength, compression strength, and load carrying capacity, compared to non-reinforced, non-metallic pipelines. The ability of FRP piping to withstand large strains allows the piping to be coiled such that long lengths can be spooled onto a reel in an open bore configuration. Spoolable FRP piping is gaining acceptance as the technology of choice for flowline installation from oil and gas wells, remediating existing (steel) flowlines, and functioning as a flexible drill pipe. Approximately one mile of continuous pipe can be spooled and later emplaced as a seamless monolith, and connection techniques for pipe segments are simple enough that they can be done in the field at the time of installation. The requirements for placement of FRP pipe are dramatically less than that for metal pipe; installation can be done in a narrow trench using light-duty earth-

moving equipment. This enables the pipe to be installed in areas where right-of-way restrictions are severe. In addition, FRP pipe can be manufactured with fiber optics, copper signal wires, power cables or capillary tubes installed directly into the structural wall of the piping. This offers the option of manufacturing the pipe with embedded sensors and operating it as a so-called smart structure. Sensors embedded in the pipe can be powered via copper wire from remote locations and real-time data from the sensors can be returned through fiber optics. This provides the unique advantage of lifetime performance monitoring of the pipe.

Approach

The challenge for adapting FRP pipeline technology to hydrogen service consists of evaluating the pipeline materials for hydrogen compatibility, developing methods for manufacturing large-diameter pipelines, developing a plastic liner with acceptably low hydrogen permeability, determining the necessary modifications to existing codes and standards to validate the safe and reliable implementation of the pipeline, and assessing the availability of sensor technology that ensures the safe and reliable use of the pipeline during its service lifetime.

The issues currently being considered are identifying the advantages and challenges of the various manufacturing methods, identifying methods and sensors for monitoring the structural health of the pipeline during its lifetime, and considering options for pipeline joining technology. The requirements for structural health monitoring and embedded real-time measurements such as gas temperature, pressure, flow rate, and pipeline leakage are being assessed. Requirements for bench-scale tests of FRP pipelines to determine their long-time compatibility with hydrogen are being prepared as well.

Work beyond the initial year will focus on advancing the materials performance beyond the proof stage, evaluation of life-cycle costs and failure modes, qualification of the materials and construction methods, integration of sensors, compliance with manufacturing codes and standards, and implementing a commercialization strategy.

Polymer-layered silicate (PLS) nanocomposites are being formulated for use as the non-permeable liner in FRP hydrogen pipelines. PLS nanocomposites are formed by mixing organo-modified clay (montmorillonite) with a polymer such as poly(ethylene) terephthalate (PET), in melt or in solution. If the polymer and modified clay are well matched for ion exchange, exfoliation of the layered clay is achieved. This exfoliated morphology is critical for achieving a dramatic decrease in hydrogen permeability in the polymer.

The intent is to optimize the organo-modifier and clay loading conditions to achieve the lowest possible permeability. Work beyond the initial year will focus on developing the best extrusion conditions and bench-scale testing of an extruded liner. Hydrogen permeability testing of PLS nanocomposite samples is being carried out in an Oak Ridge National Laboratory (ORNL) facility that allows testing at high hydrogen pressures over broad temperature ranges. The system incorporates a sample holder designed for small (~1 cm) diameter coupons of metal or ceramic, and can straightforwardly be modified for tests of polymer composite material by using an appropriate support (e.g., metal frit). In addition to the tests on hydrogen permeability, sample coupons will be mechanically tested (e.g., modulus of elasticity) before and after hydrogen exposure to assess the effects of exposure on mechanical properties.

Results

FRP Pipeline

Determining an initial cost estimate for hydrogen delivery via FRP pipeline technology, hydrogen demand for transportation use was the first step in assessing the feasibility of the technology. Hydrogen demand was obtained from technical targets and existing transportation data. The estimated demand is approximately 0.5 kg H₂ per day per capita. Natural gas pipelines deliver large quantities of energy from a limited number of sources or terminals, moving the gas cross-country in large pipelines serving tens of millions of people. To replicate this energy delivery with hydrogen would require pipelines with a diameter of several feet. Fortunately, a hydrogen economy lends itself

to a more regional infrastructure where hydrogen can be delivered using smaller diameter pipes. For this analysis we considered the case where a hydrogen generation plant is located 200 miles from the population it serves, and then estimated the pipeline sizes required to serve populations of 100,000, 1 million, and 10 million persons. Using spoolable composite piping greatly simplifies the manufacturing and installation of the pipeline. Today, spoolable composite piping is readily available in sizes up to four-inch ID, with pressure ratings to 3,000 PSI for the four-inch pipe. Larger composite pipes are contemplated and are therefore considered in this analysis. It is assumed that hydrogen enters a 200-mile long pipeline at 1,000 PSI pressure and the allowable pressure drop is 300 PSI. The implications of these assumptions are discussed later. As estimated above, time-averaged demand is assumed to be 0.5 kg H₂ per day per capita. However, as with electricity, the demand is not constant in time, so an assumption that peak demand is 1.5 times average demand was made.

Case 1: For a city population of 100,000, peak demand would be approximately 3,000 kg H₂/h. Five parallel spoolable, 4-inch diameter pipes or a single 8-inch diameter pipe will serve this city's demand.

Case 2: For a city population of 1,000,000, peak demand will be approximately 30,000 kg H₂/h. In this case, 50 parallel 4-inch diameter pipes, 9 parallel 8-inch diameter pipes, 3 parallel 12-inch diameter pipes, or a single 18-inch diameter pipe would be required.

Case 3: For a metropolitan area with a population of 10,000,000, peak demand will be about 300,000 kg H₂/h. Such a large population likely will have to be served by multiple hydrogen generating stations, so it is likely that such a large population would be served by several pipelines similar to Case 2. If it is served by a single pipeline, that line would consist of 500 parallel 4-inch diameter pipes, or 90 parallel 8-inch diameter pipes, 30 parallel 12-inch diameter pipes, or a single 44-inch diameter pipe.

The above estimates are summarized in Table 1.

Table 1. Hydrogen Pipeline Size Estimates for 1,000 PSI Source Pressure and 300 PSI Pressure Drop

Population	100,000	1,000,000	10,000,000
Peak Demand, kg/h	3,000	30,000	300,000
No. 4-inch pipes	5	50	500
No. 8-inch pipes	1	9	90
No. 12-inch pipes	N/A	3	30
Single pipe ID, inches	8	18	44

The data in Table 1 shows that either a single large pipe or many small pipes would be required to serve populations that exceed one million. This requirement can be reduced if source pressure is increased, as higher pressure increases density and therefore decreases fluid velocity for a given mass flow rate. The data in Table 2 shows the pipeline estimates if source pressure is increased to 3,600 PSI (a typical compressed natural gas fuel tank rating) with demand and allowable pressure drop unchanged. The specific energy loss is about the same for both cases.

Table 2. Hydrogen Pipeline Size Estimates for 3,600 PSI Source Pressure and 300 PSI Pressure Drop

Population	100,000	1,000,000	10,000,000
Peak Demand, kg/h	3,000	30,000	300,000
No. 4-inch pipes	3	30	300
No. 6-inch pipes	1	10	100
No. 8-inch pipes	N/A	5	46
No. 12-inch pipes	N/A	2	16
Single pipe ID, inches	6	15	36

Increasing the allowable pressure drop also reduces the required pipe size or number of pipes, but introduces the penalty of greater energy loss in transmission. Installing surge capacity in the population center could also have a very significant effect, as it reduces the peak flow rate in the

transmission pipeline. Pipeline pressure, allowable pressure drop, and surge capacity need to be studied in the context of total system economics that include the cost of pumping, storage infrastructure, and so on. The intent of the presentation of Table 2 is to demonstrate that these very simple parametric choices can significantly affect transmission cost and thus should not be made arbitrarily.

With the above analysis in mind, FRP pipe economics is very attractive, especially in regional or distributed service. FRP 4-inch, 1,000 PSI rated spoolable pipe costs about \$10 per foot installed; for 3,000 PSI pressure rating, the installation cost increases to about \$14 per foot. In both cases, installation costs are about \$2 per foot and terrain is assumed to be rural, level ground with deep soil. With allowances for installation complexity in mountainous or urban terrain, the total installed cost will range from \$10 to \$20 per foot for 4-inch diameter spoolable composite pipe. Today, spoolable piping manufacturers could install a composite pipeline to serve a 100,000 person population for a cost of \$250,000 to \$500,000 per mile (not including the cost for right-of-way), which is well below DOE's capital cost target. When one considers the opportunities for operational cost savings due to integrated health monitoring, the composite pipe is extremely attractive economically.

There also appear to be some compelling advantages associated with using a few small FRP pipes instead of one large diameter pipe. First, it allows the pipeline to continue operating at reduced capacity in case of damage to one pipe. Second, it offers the opportunity to stage capital investment by installing only one pipe to satisfy demand during the early transition period, then adding capacity as demand increases. This option is made attractive by the very low installation cost associated with spoolable FRP pipe.

A limitation on pipe diameter could be imposed by the feasibility of transporting it from the manufacturing factory. Four-inch pipe can be spooled for highway transport. Larger diameter pipe requires larger diameter spools to avoid exceeding material strain limits. In offshore applications, where the spool can be transported by barge, spoolable pipe can exceed one foot in diameter. Therefore, larger diameter spoolable FRP pipe may be an option for

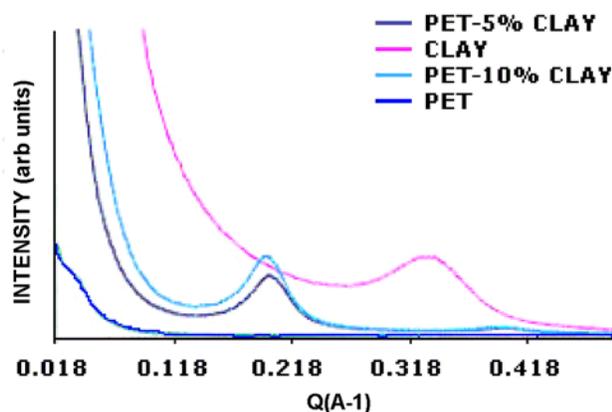


Figure 1. SAXS Profiles of PET/Clay Nanocomposites, Pure Clay and Pure PET

hydrogen pipeline infrastructure if we can determine methods for transporting it from the factory to the pipeline emplacement. At this time we have no data on costs or pressure ratings associated with spoolable pipe exceeding four inches in diameter.

Polymeric Nanocomposites with Reduced H₂ Permeance

Work on an improved liner material made from PLS nanocomposites began by solution mixing PET and organo-modified clay in phenol/chloroform mixed solvent and then stirring the mixture at elevated temperature for several hours. Two PET/clay samples with clay contents of 5 and 10 wt% were prepared in this way. After the sample solutions were thoroughly mixed, they were dried in a vacuum oven for a day or so. Films were prepared from the dried PET/clay mixtures by pressing them into thin membranes on a heated press. The dried and pressed PET/clay samples were then cut into the shapes required for post-processing analysis.

Small angle X-ray scattering analysis (SAXS) was used to determine the extent of intercalation and exfoliation in the two PET/clay mixtures. Samples of pure PET and pure organo-modified clay were also analyzed and used for comparison to the PET/clay samples. The results of the SAXS analysis are presented in Figure 1, where the graph displays the intensities of the scattered X-rays plotted as a function of the scattering vector Q . A peak in the scattering curve indicates that the sample contains a layered structure. The scattering curve for pure clay has a peak near $Q=0.3$, while the curve for the pure



Figure 2. TEM Micrograph of PET/10% Clay Nanocomposite (The clay appears as dark ridges in the lighter-shaded PET. Some intercalation of the clay platelets is evident.)

PET does not have a peak. The curves for the PET/clay samples each have peaks near $Q=0.2$. As the interlayer spacing increases, the peak shifts to smaller Q . Exfoliation of the clay platelets would result in increased random orientation of the platelets in the samples. Thus, if exfoliation had been achieved, it would be indicated by a broadening of the peak. The SAXS analysis showed that some intercalation of the silicates occurred but it gave no indication of exfoliation. This is further evidenced by transmission electron microscopy (TEM) analysis of the samples. In the TEM images shown in Figure 2, the clay appears as dark ridges in the lighter-shaded PET. The dark ridges indicate that the majority of the clay is present as intercalated clusters, with only a partial exfoliation.

To determine the decrease in hydrogen permeability attributable to the clay nanocomposites, the diffusion rates of hydrogen in thin films of pure PET and PET/10% clay were measured using the ORNL Internally Heated High Pressure facility. The results of the permeability measurements are

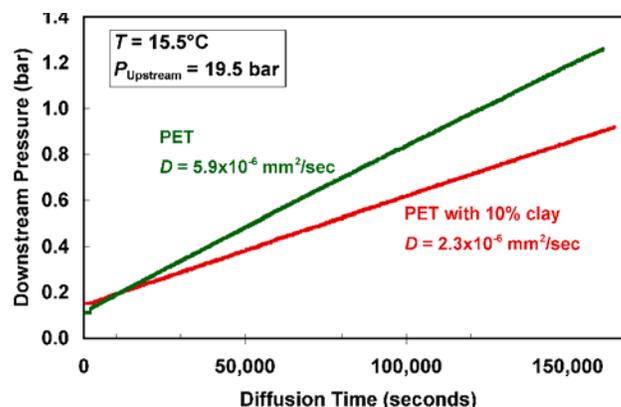


Figure 3. Hydrogen Permeation Measurements of PET and PET/10% Clay Nanocomposite

displayed in Figure 3. The diffusion rate in the PET/10% film exhibited a 60% decrease when compared to the diffusion rate in the pure PET film. This is a significant improvement in already good hydrogen barrier property of PET, and the improvement is especially remarkable because the synthesis of the PLS nanocomposites in PET was by no means optimized.

In the second formulation of PLS nanocomposites, a strategy was devised for obtaining a higher degree of exfoliation in the PET/clay samples. To this end, the partial sulfonation of poly(butylene terephthalate) technique introduced by Moore and co-workers [1] was adapted for use with PET. Dimethyl terephthalate and dimethyl 5-sulfoisophthalate sodium salt with ethylene glycol were preheated and mixed in a flask. A small amount of titanium(IV) isopropoxide catalyst was added to the mixture before the mixture temperature was further increased. The gradual application of a partial vacuum removed the extra ethylene glycol, and when most of the ethylene glycol had been removed the temperature was further increased and then the flask was evacuated at high vacuum for a couple of hours. A white solid powder of PET with 3% sulfonation was produced. Nanocomposites were prepared in this sulfonated PET by solution mixing, and films were pressed at high temperature and pressure as before. Two PET/clay samples with clay contents of 5 and 10 wt% were prepared.

SAXS was used to determine the extent of intercalation and exfoliation in the sulfonated PET/clay mixtures. The results of the analysis are

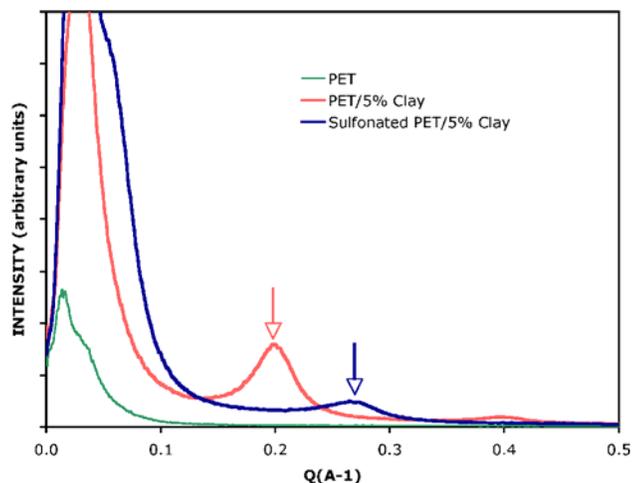


Figure 4. SAXS Profile of Sulfonated PET/Clay Nanocomposites with 5 wt% Clay Loading

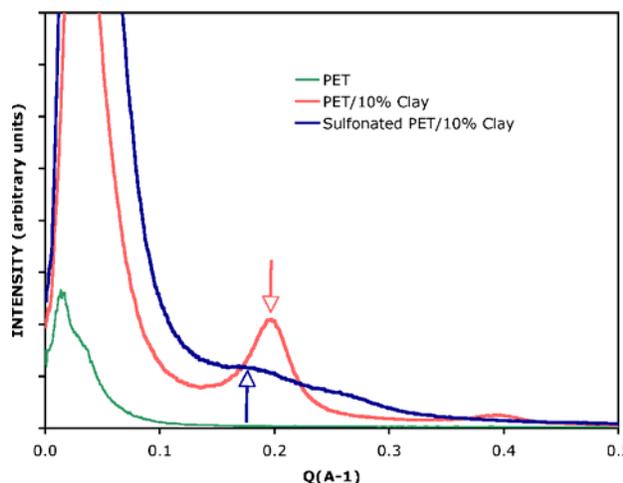


Figure 5. SAXS Profile of Sulfonated PET/Clay Nanocomposites with 10 wt% Clay Loading

presented in Figures 4 and 5, where the sulfonated PET/clay mixtures are compared with the results obtained earlier from the (non-sulfonated) PET/clay mixtures. The presence of the peaks in the SAXS curves (designated by arrows) is an indication that intercalation of the clay platelets has occurred in both mixtures. The peak in the sulfonated PET/clay mixtures has broadened, and this broadening is a strong indicator that exfoliation of the platelets has occurred.

Permeability measurements of the sulfonated PET/clay mixtures will be done in the near future.

Conclusions

- The use of multiple small-diameter FRP pipelines for hydrogen transmission is practically and economically feasible.
- PLS nanocomposites can be synthesized in PET using organo-modified clay.
- The presence of clay platelets in modified PET provides a dramatic decrease in hydrogen permeability, compared to unmodified PET.

FY 2005 Publications/Presentations

1. "New Materials for Hydrogen Pipelines," Poster PDP-51, presented at the 2005 DOE Hydrogen Program Review, May 23-26, 2005, Arlington, Virginia.

References

1. B. J. Chisholm, R. B. Moore, et al., *Macromolecules*, 35 5508 (2002).