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**Texas Commission on Environmental Quality
New Technology Research & Development (NTRD) Program
Monthly Project Status Report**

Contract Number: 582-5-65591-0002

Grantee: The University of Texas at Austin

Date Submitted: September 26, 2005

Report for the **Monthly** period:

Starting Date: August 1, 2005 Ending Date: August 31, 2005

Section I. Accomplishments (*Please provide a bulleted list of project accomplishments as well as a description of their importance to the project.*)

PROJECT OBJECTIVES

The overall objective of this project is to develop cost-effective, high-temperature gas separation membranes for producing inexpensive, high-purity hydrogen (H₂) from synthesis gas generated by steam reforming or gasification of fossil fuels. The two specific technical objectives of the project are:

- (i) To develop polymeric and/or polymer-based nanocomposite membranes with high H₂ permeability, high H₂/carbon monoxide (CO) and H₂/carbon dioxide (CO₂) selectivities, and high thermal stability up to 250-300 °C.
- (ii) To demonstrate the technical and economic feasibility of using such membranes for producing low-cost fuel-cell-quality H₂ from synthesis gas streams.

PROJECT ACTIVITIES AND STATUS

The Grant Activities for the project consist of seven (7) tasks. The project accomplishments during this report period are summarized in the bulleted list below.

UT

- **Nanocomposite Membrane Testing:** Pure-gas permeation testing was performed at 35 °C on the 3 vol% Ni/Ultem[®] 1000 nanocomposite membrane. Pure-gas permeation characterization of nanocomposite membranes is important for understanding how nanoparticle addition affects the gas transport properties of the base polymers. (*Project Task 2*)
- **Thermal Property Characterization:** The glass transition (softening) temperature of Ultem 1000 nanocomposite membranes filled with 0, 5, 10 and 15 vol% SiO₂ nanoparticles were investigated using differential scanning calorimetry (DSC). The DSC tests are useful because they provide important information on the upper temperature limits at which the nanocomposites may be used in practice and show how the addition and concentration of SiO₂ particles influence the softening temperature of the base polymers.

RTI

- **PBI Membrane Preparation:** Ongoing preparation of free-standing, dense polybenzimidazole (PBI)/silica nanocomposite films continued by using two techniques: (i) knife-casting SiO₂-particle-doped PBI solutions onto glass plates and (ii) casting these solutions into glass rings supported on glass plates. Casting-knife gap used was increased to make thicker films because initial thinner (6- to 8- μ m-thick) films obtained using smaller gaps were found to be defective (e.g., pinholes). Films were thus made with a 10-mil knife gap, resulting in an average dry film thickness of \sim 20 μ m. The glass ring method was also used to successfully make films of similar thickness with good durability.

As shown by earlier thermogravimetric analysis (TGA) data, measurable amounts of residual DMAc solvent as well as moisture tenaciously remained in PBI-based membranes dried at 70-100 °C. More aggressive drying or post-heat treatment procedures are therefore needed because the presence of measurable amounts of solvent/moisture could significantly impact the intrinsic membrane permeation properties measured. Thus, our PBI-based membrane drying procedure was tentatively modified to include a 250 °C post-heat treatment step for 18-20 h under N₂ after the bulk drying step (70 °C under N₂ for 24 h).

Efforts also continued on preparing trial PBI composite (multilayered) membranes on a Mott Corporation 316L stainless steel support with 0.5- μ m pore size. Thin PBI layers were deposited onto the support substrate by knife-casting and manual coating/spreading of a PBI solution (14 wt% in DMAc [*N,N*-dimethylacetamide]). These trial PBI coatings will indicate whether the 0.5- μ m stainless steel substrate is a viable option to use for PBI composite membranes.

Making good (defect-free) PBI membranes in both thin-film composite membrane form and inorganic-particle-filled nanocomposite form is a critical step in the development of gas separation membranes for this project. (**Project Task 1**)

- **Membrane Permeation Testing:** Pure H₂ and CO₂ permeation properties were measured at room temperature over a feed pressure range of 100-300 psig for 19- and 34- μ m-thick PBI films. At 23 °C, these pure PBI films exhibited very low permeability (1.2-1.7 barrer for pure H₂; 0.2-0.25 barrer for pure CO₂) and a pure H₂/CO₂ selectivity of 6-7. Unfortunately, further permeation-testing of these films as a function of temperature and/or with a syngas mixture had to be aborted because they became defective during testing. Additionally, the pure H₂ and CO₂ permeation properties of the tubular PBI composite membrane module was measured at feed pressures of 100, 200, and 300 psig over a temperature range of 23-200 °C. The module data will be analyzed and reported next month.

Knowledge of the gas transport properties of pure PBI and other high-temperature-resistant polymers is important because gas permeability/selectivity information, especially for the syngas species to be separated in this project, is scarce in the literature for these polymers. The intrinsic separation properties of these pure polymers are also important because they will be the base values to which the permeation data for the corresponding nanocomposites will be compared to understand the effect of nanofiller addition and against which the permeation data for thin-film polymer composite membranes will be gauged to verify how good is the composite membrane separation performance. (**Project Task 2**)

- **Thermal Property Characterization:** TGA tests in a *syngas mixture* environment of H₂, CO₂, and CO were completed on pure Ultem 1000 polyetherimide (PEI) and SiO₂-filled Ultem 1000 nanocomposite blend films. By performing TGA in syngas, a more realistic evaluation of material thermal stability under conditions closer to those of the actual application is obtained. Additionally, to gauge whether a 250 °C post-heat treatment could achieve complete removal of residual solvent/moisture from the membranes, TGA experiments were performed on PBI-based membranes that had undergone this high-temperature treatment step for 18-24 h under N₂. The TGA studies are important for determining the thermal stability (or limitations) of the neat polymer

membranes and polymer-based nanocomposite membranes being developed for the targeted high-temperature gas separation application. (*Project Task 4*)

Specific results and details of this period's project activities are discussed on a task-by-task basis below.

Indicate which part of the Grant Activities as defined in the grant agreement, the above accomplishments are related to:

TASK 1: Prepare High-Temperature Membranes

UT

No new nanocomposite membrane films were prepared at UT during this period.

RTI

In this ongoing task, two casting techniques were retried to make additional dense polybenzimidazole (PBI)/silica nanocomposite films with improved mechanical properties. For these films, the various PBI solutions loaded with Aldrich 10-nm SiO₂ and prepared last month were used. In one method, the nanoparticle/polymer solution mixtures were knife-cast using a 10-mil knife gap to produce membranes with a dry film thickness of ~20 μm. This casting-knife gap is roughly two times larger than that used to make the earlier 6- to 8-μm-thick membranes, which were defective due to pinholes. Thicker, free-standing films tend to have less pinhole defects and, thus, are useful at this project stage for obtaining intrinsic material properties. In the second approach, the nanoparticle/polymer solution mixtures were cast into glass rings supported on glass plates. Previously, membrane films made by this glass-ring method were so thick that they experienced severe drying stresses and became sufficiently rigid to exhibit fairly brittle behavior. However, by careful casting of the particle/polymer mixture into the glass ring, we succeeded in making films thin enough to be flexible yet thick enough to be fairly robust and easily handled.

Additionally, the film drying procedure was tentatively modified in light of recent thermogravimetric analysis (TGA) data that indicated the presence of measurable amounts of residual solvent and/or moisture in the PBI-based membranes. The drying procedure now includes a post-heat treatment step at an intermediate high temperature well below the PBI degradation temperature. First, bulk drying of solvent-cast films occurs for 24 h in a 70 °C oven with N₂ purge. After the essentially dry films are removed from the glass casting surface, they are returned to the oven at 250 °C for another 18-20 h under N₂. In Task 4 this month (described below), the effectiveness of this post-heat treatment step is examined more closely.

"Proof-of-concept" coatings of pure PBI onto a microporous 316L stainless steel support (Mott Corporation) were also performed to determine whether this metal substrate is a viable option to use for making thin-film PBI composite (multilayered) membranes. The porous stainless steel substrate tried had a 0.5-μm pore size. The first PBI coating attempt used the knife-casting technique with the knife gap essentially zeroed to the substrate thickness. Because the substrate was not perfectly flat, there were regions where the PBI solution coating did not cover the support surface. Furthermore, after heating at 70 °C for 24 h, most of the PBI layer appeared to absorb into the substrate. The only evidence that a coating had been applied was indicated by a slight darkening of the metal support surface. In our second attempt, a small quantity of PBI solution was poured onto the substrate and coated (spread out) manually to cover the entire support. The resulting coating layer was thicker than that in the first attempt. After drying overnight at 70 °C, a film of PBI was found only on the substrate section where the polymer solution coating had initially been thickest. Another layer of PBI solution was then deposited on top of the first layer. This second PBI layer allowed for complete coverage of the substrate surface after drying so a third PBI coating layer was not applied. We have yet to determine how defect-free is the resulting double-coated PBI membrane layer on the microporous stainless steel substrate.

TASK 2: Evaluate Membrane Permeation Properties

UT

A nanocomposite film of Ultem[®] 1000 containing 3 vol% Ni nanoparticles was tested with pure gases. Its pure-gas permeabilities are shown and compared to the permeation properties of the pure (unfilled) Ultem 1000 film in Table 1. Please note that, next month, the CO₂ permeability, which was either below the resolution of the testing equipment or improperly tested, will be remeasured.

Table 1. Pure-Gas Permeability of Unfilled Ultem 1000 and a Ni-Filled Ultem 1000 Nanocomposite Blend at 35 °C

Sample	Permeability (barrer) [Penetrant size (Å)]				
	H ₂ [2.89]	O ₂ [3.46]	N ₂ [3.64]	CH ₄ [3.8]	CO ₂ [3.3]
Ultem 1000 ^a	9.4	0.76	0.14	0.03	3.3
3 vol% nano-Ni + Ultem 1000 ^b	8.0	--	--	0.14	--

$$1 \text{ barrer} = 10^{-10} \text{ cm}^3(\text{STP}) \cdot \text{cm}/(\text{cm}^2 \cdot \text{s} \cdot \text{cmHg})$$

$$\Delta p = 3.4 \text{ atm (50 psi)}$$

^a Data from May 2005 monthly report

^b Ni nanoparticle size = 20 nm

RTI

Pure H₂ and CO₂ permeation properties of a 19- μm -thick Celazole PBI film (Sample #A1) and a 34- μm -thick Pall PBI film (Sample #B1) were measured at 23 °C over a feed pressure range of 100-300 psig. These data are presented in Table 2. Both PBI films have a pure H₂/CO₂ selectivity of 6-7 and very low permeability (1.2-1.7 barrer for pure H₂; 0.2-0.25 barrer for pure CO₂). Continued characterization of these two films at higher temperatures and/or with a syngas feed could not be done because they became defective upon further testing.

The tubular PBI composite membrane module received from Pall Corporation was also evaluated with pure H₂ and CO₂ this period. The feed pressures used in module permeation tests were 100, 200, and 300 psig. The module test temperature varied from 23 to 200 °C. The permeation data collected for the module will be analyzed and reported next period.

Table 2. Pure H₂ and CO₂ Permeation Properties Measured for Two Dense PBI Films at 23 °C

PBI film	Feed pressure (psig)	Pure-gas permeability (barrer)		Pure H ₂ /CO ₂ selectivity
		H ₂	CO ₂	
Sample #A1	100	1.2	— ^a	—
	201	1.2	0.20	6.0
	300	1.4	0.20 ^b	7.0
Sample #B1	100	1.7	— ^a	—
	200	1.5	0.25	6.0
	304	1.4 ^b	0.20	7.0

1 barrer = 10⁻¹⁰ cm³(STP)·cm/(cm²·s·cmHg)

Samples #A1 and #B1 were made last month by the glass-ring casting method from 14 wt% and 15 wt% PBI solutions, respectively, in DMAc and dried for 24 h under N₂ at 70 °C.

Film thickness = 19 μm (Sample #A1); 34 μm (Sample #B1)

Permeate pressure = 0 psig; Downstream He sweep rate = 14-43 cm³/min

^a Too low to be measured (determined) on permeation system used.

^b Actual feed pressure used = 301 psig.

TASK 3: Evaluate Membrane Reactor Properties

RTI

This task has not yet started at RTI.

TASK 4: Characterize Thermal and Morphological Properties of Membranes

UT

Membrane films of pure Ultem 1000 and Ultem 1000 doped with various concentrations of SiO₂ nanoparticles were characterized using differential scanning calorimetry (DSC). Representative DSC data collected on these samples are shown in Figure 1 for the Ultem membrane filled with 5 vol% SiO₂ nanoparticles. From the DSC results, the unfilled Ultem film has a glass transition temperature T_g of 210 °C, which is consistent with the T_g of ~209 °C reported in the literature.¹ Addition of SiO₂ nanoparticles increases the T_g by about 10 °C, even at loadings as low as 5 vol%. As nanoparticle loadings increase from 5 to 15 vol% SiO₂, the T_g of the Ultem nanocomposites decreases slightly from 220 °C to 218 °C, respectively (cf. Figure 2).

¹ Vu, D. Q.; Koros, W. J.; Miller, S. J., *J. Membr. Sci.* **2003**, 211, 311-334.

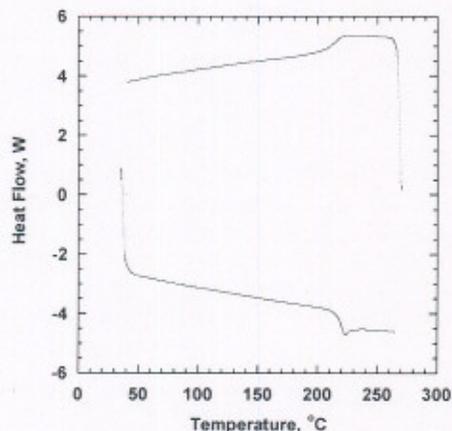


Figure 1. DSC sweep for Ultem 1000 filled with 5 vol% SiO₂ nanoparticles. Heating rate was 20 °C/min.

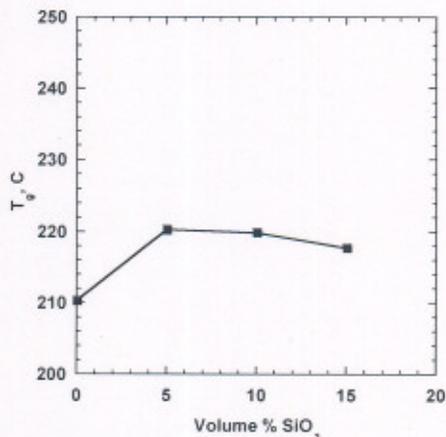


Figure 2. Effect of SiO₂ nanoparticle loading on T_g (glass transition temperature) of Ultem 1000. Data collected by DSC at a heating rate of 20 °C/min.

RTI

Because the membranes in this project are being developed for use in a syngas environment, a more realistic evaluation of their thermal stability behavior would be to conduct TGA tests in a syngas mixture. Therefore, TGA studies in a reducing syngas atmosphere of 38.4% H₂, 14.8% CO₂, and 46.8% CO were completed this month on pure Ultem 1000 PEI film and Ultem 1000 nanocomposites loaded with 5, 10, 15, and 20 vol% Aldrich 10-nm SiO₂ nanoparticles. As for the TGA experiments in helium last month, a dual-scan protocol was used for the analogous studies in syngas. To remove moisture and solvent, TGA Scan #1 was done in *helium* by heating samples from room temperature to 250 °C, holding them at 250 °C for 30 min, and then cooling them to room temperature. Immediately following the cooling step in helium, TGA Scan #2 then heated the samples in *syngas* from room temperature to 750 °C and held them at this final temperature for 30 min. In both Scans #1 and #2, a 10 °C/min heating rate was used.

The TGA results for pure Ultem 1000 and the Ultem 1000/silica nanocomposites in the syngas environment are plotted in Figure 3. Relative to that for pure Ultem, the point of rapid weight loss (i.e., rapid thermal degradation) for the SiO₂-filled Ultem nanocomposites is shifted slightly to the right toward higher temperatures. As a result, the decomposition onset temperature is a little higher for the Ultem/SiO₂ nanocomposites (~506-508 °C) than for pure Ultem (~502 °C). The thermal stability of Ultem in syngas is thus improved slightly by SiO₂ nanofiller addition, in agreement with the previous conclusion made on the basis of their TGA data in helium.

Figure 4 and Table 3 directly compare the thermal behavior of the Ultem-based membranes in syngas and inert helium environments. The onset of rapid weight loss appears to be consistently shifted slightly to the left toward lower temperatures for TGA curves in syngas relative to those in inert gas. Closer analysis of the data shows that the decomposition temperature for Ultem and its nanocomposite blends with silica is about 8-13 °C lower in syngas than in helium. Though small, this temperature difference indicates that Ultem-derived films are slightly less thermally stable in a reducing gas environment.

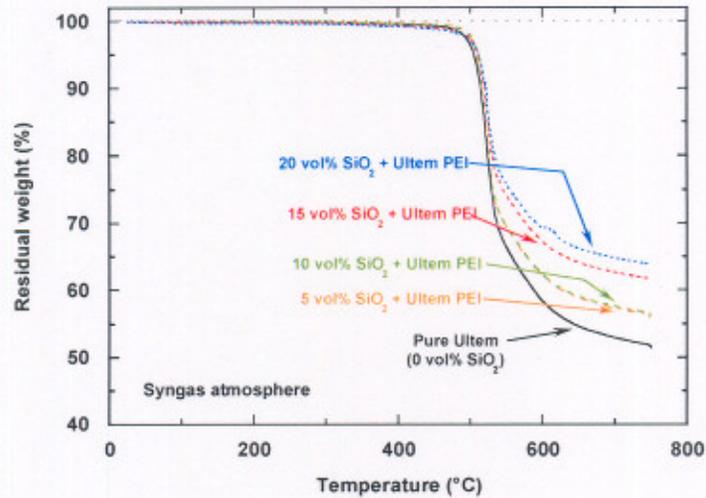


Figure 3. TGA weight loss curves for Ultem 1000 PEI nanocomposites doped with 0, 5, 10, 15, and 20 vol% Aldrich 10-nm SiO_2 nanoparticles in syngas environment of 38.4% H_2 , 14.8% CO_2 , and balance CO . Samples were heated in syngas at $10^\circ\text{C}/\text{min}$ from room temperature to 750°C according to the TGA protocol described in this report. Initial sample weights in syngas: 13.5816 mg for pure Ultem (0 vol% SiO_2); 23.1077 mg for 5 vol% SiO_2 ; 25.8519 mg for 10 vol% SiO_2 ; 29.0692 mg for 15 vol% SiO_2 ; and 33.9031 mg for 20 vol% SiO_2 .

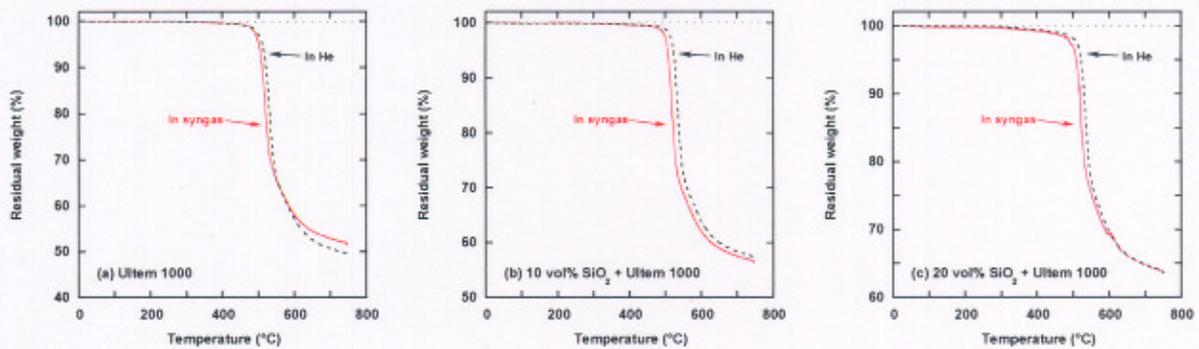


Figure 4. Comparison of TGA weight loss profiles in syngas and inert helium atmospheres for (a) pure Ultem 1000 and nanocomposite blends of (b) 10 vol% SiO_2 + Ultem 1000 and (c) 20 vol% SiO_2 + Ultem 1000. Samples were heated at $10^\circ\text{C}/\text{min}$ according to the TGA protocol described in this report (syngas results) and the July 2005 report (He results). Syngas composition used: 38.4% H_2 , 14.8% CO_2 , and balance CO . Aldrich SiO_2 nanoparticles used had a 10-nm primary particle diameter.

Table 3. Comparison of Decomposition Onset Temperatures Measured in Syngas and Inert Helium Atmospheres for Pure Ultem 1000 PEI and SiO₂/Ultem 1000 PEI Blend Nanocomposites

Sample	Decomposition onset T ^a (°C)	
	In syngas ^b	In helium ^c
Pure Ultem 1000 PEI		
This study	502	510
Literature data	— ^e	550 ^f
5 vol% SiO ₂ ^d + Ultem 1000	506	519
10 vol% SiO ₂ ^d + Ultem 1000	508	519
15 vol% SiO ₂ ^d + Ultem 1000	507	518
20 vol% SiO ₂ ^d + Ultem 1000	507	519

^a Determined by TGA at 10 °C/min heating rate.

^b Ternary syngas composition: 38.4% H₂, 14.8% CO₂, Balance CO.

^c Results from the June and/or July 2005 monthly reports.

^d Hygroscopic, untreated, 10-nm silica nanopowder from Aldrich.

^e Not available in the literature.

^f For an unspecified grade of PEI from Sepe, M. P., *Thermal Analysis of Polymers*, Rapra Review Report 95, Rapra Technology Ltd.: Shrewsbury, UK, 1997, Vol. 8, No. 11, p 17.

According to recent TGA data, measurable amounts of residual solvent/moisture are apparently left in our solution-cast PBI-based membranes. TGA results suggest that the combined amount of residual solvent and moisture present is in the range of 16-20 wt%, which may significantly affect membrane permeation properties. To drive off this leftover solvent/moisture, a pure PBI film and a 10 wt% SiO₂/PBI blend film were subjected to a post-heat treatment step at 250 °C for 18-20 h under N₂. TGA testing in helium was then conducted on these samples to determine the effectiveness of this high-temperature post-treatment on completely removing leftover moisture/solvent. The dual-scan TGA results for the post-heat-treated PBI-based samples are compared to that for the same samples with no post-heat treatment in Figure 5.

Only about half of the leftover moisture/solvent is removed by post-heat-treating the PBI-based membranes at 250 °C for 18-20 h. For the pure PBI sample, the TGA Scan #1 weight loss is ~23% with no post-treatment and ~11% with post-treatment. The Scan #1 weight loss is similar for the 10 wt% SiO₂/PBI nanocomposite: 21% and 10% without and with post-treatment, respectively. Thus, it appears that, to fully remove moisture/solvent, either a longer 250 °C post-heat treatment time period or a higher post-treatment temperature (e.g., 350 °C) would be needed. Next month, we will determine how effective a 350 °C post-heat treatment step is at driving off all moisture/solvent from PBI-based films.

An additional observation is that high-temperature post-treatment does not affect the final decomposition temperature of the PBI-based membranes. As shown in Figure 5, the degradation onset temperature is about 566-567 °C and 568-570 °C for the pure PBI and 10 wt% SiO₂/PBI blend samples, respectively, regardless of whether a post-treatment was done.

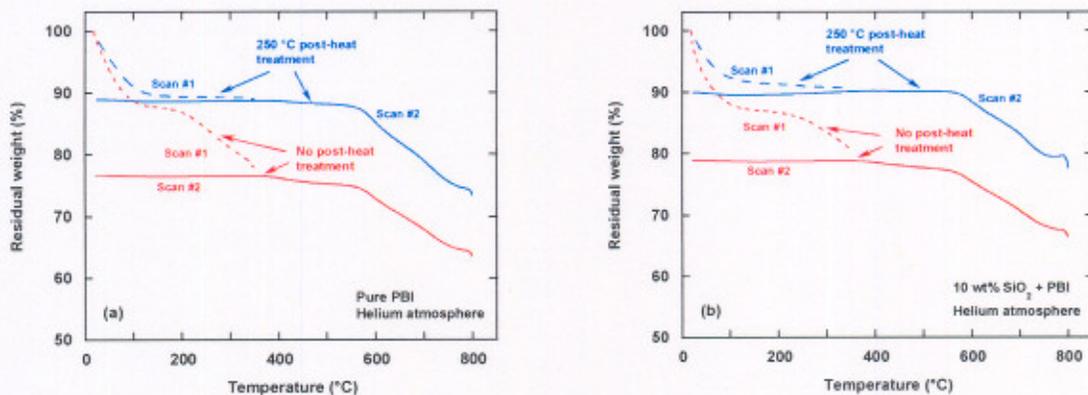


Figure 5. TGA weight loss curves showing amount of residual moisture/solvent remaining in (a) pure PBI films and (b) 10 wt% Aldrich 10-nm SiO₂ + PBI nanocomposite films with and without a 250 °C post-heat treatment step in N₂ after film drying. A single TGA test consisted of two back-to-back scans conducted in He. TGA Scan #1 heated at 10 °C/min from room temperature to 350 °C, held at 350 °C for 30 min for residual moisture and solvent removal, and then cooled to room temperature. TGA Scan #2 heated at 10 °C/min from room temperature to 800 °C and held at 800 °C for 30-60 min. All films, solvent-cast from DMAc, had been dried for 24 h under N₂ at 70 °C. Initial sample weights: 3.88454 and 4.76919 mg for pure PBI films with and without post-heat treatment, respectively; 0.981027 and 3.90413 mg for SiO₂/PBI nanocomposites with and without post-heat treatment, respectively.

TASK 5: Prepare Integrated System Process Design

RTI

This task is not yet scheduled to begin at RTI.

TASK 6: Perform Technical and Economic Analysis/Develop Commercialization Strategy

RTI

This task is not yet scheduled to begin at RTI.

TASK 7: Manage Project/Prepare Reports

UT/RTI

The seventh monthly project report was prepared.

Section II: Problems/Solutions

<p>Problem(s) Identified</p> <p><i>(Please report anticipated or unanticipated problem(s) encountered and its effect on the progress of the project)</i></p>	<p><u>UT</u></p> <p>No major problems were encountered this period.</p> <p><u>RTI</u></p> <p>No major problems were encountered this period.</p>
<p>Proposed Solution(s)</p> <p><i>(Please report any possible solution(s) to the problem(s) that were considered/encountered)</i></p>	<p><u>UT</u></p> <p>N/A this period.</p> <p><u>RTI</u></p> <p>N/A this period.</p>
<p>Action(s) Conducted and Results</p> <p><i>(Please describe the action(s) taken to resolve the problem(s) and its effect)</i></p>	<p><u>UT</u></p> <p>N/A this period.</p> <p><u>RTI</u></p> <p>N/A this period.</p>

Section III. **Goals and Issues for Succeeding Period:** *(Please provide a brief description of the goal(s) you hope to realize in the coming period and identify any notable challenges that can be foreseen)*

UT

In September, we will resolve the Ni nanoparticle dispersion difficulty in Ultem 1000 casting solutions, continue to characterize the pure-gas permeation properties of Ni/Ultem nanocomposite films, and conduct DSC tests on all appropriate Ultem-based nanocomposites. Ordering of the parts needed to build a high-temperature permeation system at UT for this project (cf. June 2005 monthly report) will also be completed, and construction of this permeation system will begin.

RTI

Next period, we will continue to characterize the gas permeation properties of pure PBI membranes and begin to evaluate those of PBI/silica nanocomposite membranes with pure H₂ and CO₂ and a syngas mixture as a function of feed pressure and/or temperature (up to 300 °C). The permeation data collected for the PBI composite membrane module will be analyzed. Additionally, four novel, highly thermally stable polybenzoxazole (PBO)-based membranes received from UT at the end of July will be permeation-tested at RTI within the next couple of months.

TGA studies in helium will also be performed next month on the PBO-based membranes to characterize their thermal stability. Furthermore, the effectiveness of a higher-temperature (i.e., 350 °C) post-heat treatment step for completely removing leftover moisture/solvent in the PBI-based membranes will be examined. TGA tests similar to those done this period on 250 °C post-treated samples will then be

conducted on these membranes to gauge the effectiveness of the 350 °C conditioning step. If time permits, TGA studies on PBI and its nanocomposites in syngas will be started.

Benny Freeman

Authorized Project Representative's Signature

Date: September 26, 2005

NOTE: *Please attach any additional information that you feel should be a part of your report or that may be required to meet the deliverable requirements for tasks completed during this reporting period.*