

## **NTRD Program Disclaimers**

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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: May 11, 2005

Report for the **Monthly** period:

Starting Date: April 1, 2005 Ending Date: April 30, 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 (H<sub>2</sub>) 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 H<sub>2</sub> permeability, high H<sub>2</sub>/carbon monoxide (CO) and H<sub>2</sub>/carbon dioxide (CO<sub>2</sub>) 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 H<sub>2</sub> 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

- Ultem<sup>®</sup> Nanocomposite Membrane Preparation: Ultem 1000 nanocomposite films were cast with MgO and SiO<sub>2</sub> nanoparticles having a primary particle diameter of 2.5 and 10 nm, respectively. Because SiO<sub>2</sub> particles disperse more uniformly than MgO particles in this polymer matrix, subsequent research in this project will focus more on the Ultem 1000 nanocomposite filled with SiO<sub>2</sub>. The demonstration of SiO<sub>2</sub> nanoparticle dispersion in Ultem<sup>®</sup> 1000 allows the project to progress to preparing nanaoparticle-filled membranes and begin the high temperature testing of these materials. **(Project Task 1)**
- Ultem Nanocomposite Membrane Testing: Ultem membranes prepared with MgO and SiO<sub>2</sub> nanoparticles were characterized with pure gases at 35 °C and 50 psig feed pressure. These experiments demonstrate the feasibility of making defect free nanocomposite films in preparation for the high temperature permeation experiments. **(Project Task 2)**

## RTI

- PBI Polymer Acquisition: In accordance with the Agreement for PBI Polymer or Solution Use between Celanese Advanced Materials, Inc. (CAMI) and RTI, the Celazole<sup>®</sup> PBI (polybenzimidazole) polymer ordered from CAMI was received. The acquisition of PBI is important because PBI is one of the key thermally stable polymers with attractive H<sub>2</sub> separation properties to be developed into useful membranes in this project. **(Project Task 1)**
- PBI Casting Solutions: Preparation of Celazole PBI casting solutions was only partially successful. Solutions containing 5, 10, and 15 wt% polymer in *N,N*-dimethylacetamide (DMAc), a known solvent for this material, were attempted. Partial dissolution of PBI was eventually achieved by stirring the polymer-solvent mixtures in a hot (95 °C) water bath. On the basis of the viscosity observed for the semi-dissolved solutions, a practical polymer concentration for making solution-cast membranes appears to be ~10-15 wt%.

To dissolve PBI completely in DMAc, more elevated temperatures (e.g., 150-260 °C) will be tried next month. Such high dissolution temperatures can be reached by using a silicone oil heating bath, and supplies (silicone oil bath fluid, beakers, thermometers, etc.) for this task were ordered. The proper preparation of PBI solutions is important because the solutions will be used to form thermally stable PBI membranes with and without nanoparticles for the project. Therefore, it is important to determine the appropriate polymer dissolution conditions and a desirable polymer concentration to use for PBI membrane preparation. **(Project Task 1)**

- PBI Film Preparation: A trial Celazole PBI film was cast from the partially dissolved 15 wt% polymer solution prepared. This cast film is currently drying in the fume hood at ambient conditions. Determining the proper film casting and drying conditions are important for making good (defect-free) PBI films as gas separation membranes for the project. **(Project Task 1)**
- PBI Membrane Module: Testing of the tubular PBI composite membrane module has been rescheduled for the next period due to a suspected subtle leak in the permeation test system, which was reconfigured last month for the project (*see bulleted item below*). Determination of the H<sub>2</sub> separation properties of this PBI composite membrane is important because it will provide a separation-performance reference point based on a current state-of-the-art thin-film PBI membrane that is in a form readily packageable and scaleable into a useful industrial membrane module. Membrane performance data obtained on this first PBI composite membrane tube will be used to guide the ensuing development steps on how thin to make the selective PBI layer on microporous supports so that the optimal combination of high H<sub>2</sub> selectivity and high H<sub>2</sub> productivity (flux) for this membrane can be obtained for the application of interest. These data will also be helpful in guiding the development of potentially high-performance PBI nanocomposite membranes through addition of nanoparticles into the polymer matrix. **(Project Task 2)**
- Gas Permeation System: Validation data collected last period on polymer membrane standards in the reconfigured permeation system were analyzed and showed that the system was giving unacceptable values that were outside the experimental error range. Gas fluxes and selectivities measured on the membrane standards were much lower than past values obtained on the same or similar samples by the same permeation technique. The permeation system is currently undergoing troubleshooting to locate the cause(s) of this problem. It is suspected that the system has a subtle leak, which would be further magnified in the data the lower the permeability (flux) of the membrane tested. The system validation step is important to the project because it ensures that the permeation system will operate properly and generate accurate gas permeation data on the membranes to be tested. **(Project Task 2)**

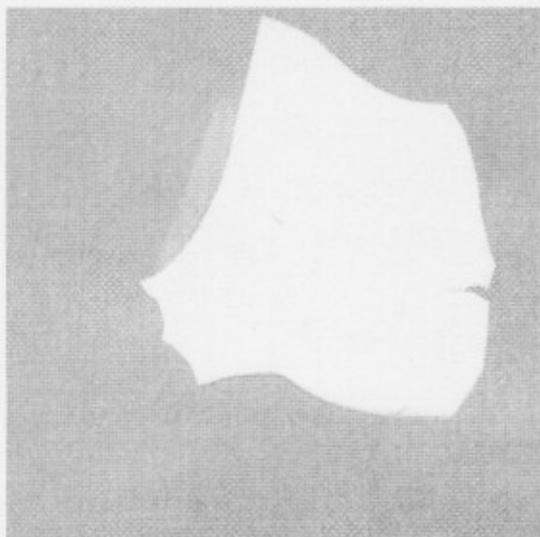
Specific results and details of this period's project activities are discussed on a task-by-task basis below.

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**

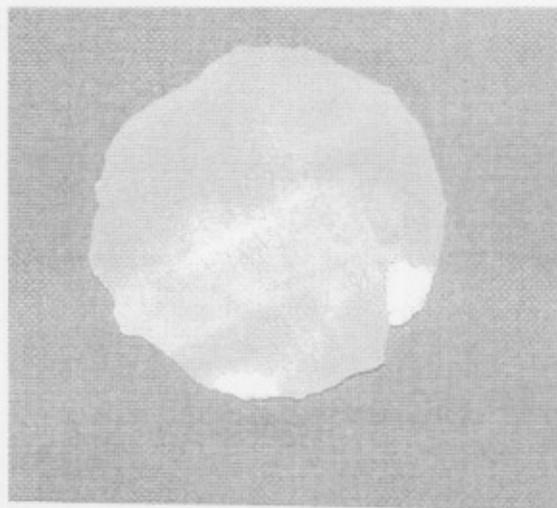
UT

During this period, Ultem<sup>®</sup> 1000 nanocomposite films were cast with MgO and SiO<sub>2</sub> nanoparticles having a primary particle diameter of 2.5 and 10 nm, respectively. It appears that SiO<sub>2</sub> disperses more uniformly in Ultem 1000 than MgO, as shown in Figures 1a and 1b. Even at higher loadings (i.e., 20 vol%), the SiO<sub>2</sub> nanoparticles do not appear to form agglomerates, whereas such agglomerates are visible in MgO-filled nanocomposites at lower loadings (i.e., 13 vol%) [yellow arrows in Figure 1b]. In the coming months, our research will focus on SiO<sub>2</sub>-filled Ultem 1000 due to superior dispersion of these nanoparticles in this polymer matrix.



Ultem<sup>®</sup> 1000  
(20 volume % SiO<sub>2</sub>)

**Figure 1a.** Photograph of Ultem 1000 filled with 20 nominal volume % SiO<sub>2</sub> nanoparticles of 10-nm primary particle diameter.



Ultem<sup>®</sup> 1000  
(13 volume % MgO)

**Figure 1b.** Photograph of Ultem 1000 filled with 13 volume % MgO nanoparticles of 2.5-nm primary particle diameter. Yellow arrows indicate a regions of high nanoparticle concentration relative to majority of the nanocomposite.

RTI

Membrane casting solutions were prepared with partial success from Celazole<sup>®</sup> PBI (polybenzimidazole) powder, of which ~1 pound was received this month from Celanese Advanced Materials, Inc. (CAMI). The Celazole polymer acquired is a bronze 100-mesh (sub-149- $\mu$ m) powder. Solutions were made with 5, 10, and 15 wt% PBI in *N,N*-dimethylacetamide (DMAc). At room

temperature, the PBI showed no signs of dissolving in DMAc after 2 days of mixing. Therefore, the olive-brown polymer-solvent mixture was placed in a hot (95 °C) water bath, and partial dissolution of PBI was achieved after about 1 day of stirring at this higher temperature. Longer times in the hot water bath did not noticeably increase the degree of polymer dissolution. The partially dissolved PBI in DMAc solutions were a dark golden brown. As expected, solution viscosity increased with increasing polymer concentration. On the basis of solution viscosity, a good polymer concentration for casting into membranes seems to be about 10-15 wt%.

More aggressive dissolution conditions (e.g., temperatures higher than 95 °C) are apparently needed to completely dissolve this commercial Celazole grade of PBI. To obtain higher bath temperatures for dissolution, one approach is to use a silicone oil heating bath. Supplies, including high-temperature silicone oil bath fluid, beakers, and thermometers, were thus ordered so that higher dissolution temperatures of 150-260 °C can be tried next.

The partially dissolved 15 wt% PBI solution was filtered once with a syringe filter to remove most of the undissolved solids. This filtered solution was then cast into a glass ring supported by a glass plate to make a membrane film. The cast film is currently drying at ambient conditions in the fume hood. If necessary, it will be transferred to a warm oven to facilitate the drying process as well as to minimize exposure to ambient moisture, which may interfere with proper drying of the sample into a dense film.

## **TASK 2: Evaluate Membrane Permeation Properties**

### UT

Permeation properties of the materials in Task 1 were tested with pure CO<sub>2</sub>, N<sub>2</sub>, O<sub>2</sub>, H<sub>2</sub>, and CH<sub>4</sub>. For both MgO- and SiO<sub>2</sub>-filled nanocomposite membranes, gas permeability is substantially higher than the unfilled polymer. The extent of permeability enhancement appears to be related to the size of the penetrant molecules. As shown in Table 1, the permeability of CO<sub>2</sub>, the smallest molecule for which we have comparable data, increases by 300-600% as particle loading increases, and the permeability of CH<sub>4</sub>, the largest penetrant molecule tested so far, is 15 to 20 times higher in a film containing nanoparticles than in a film without particles.

**Table 1.** Preliminary Permeation Data for Ultem 1000 Nanocomposites

Sample	Permeability [Penetrant size Å] <sup>2</sup> (Barrer)				
	H <sub>2</sub> [2.89]	O <sub>2</sub> [3.46]	N <sub>2</sub> [3.64]	CH <sub>4</sub> [3.8]	CO <sub>2</sub> [3.3]
Ultem 1000 <sup>1</sup>	—	0.38	0.05	0.04	1.45
Ultem 1000 with 7 vol% MgO	16.9	2.5	0.74	0.62	6.0
Ultem 1000 with 20 vol% SiO <sub>2</sub>	17.5	2.2	0.64	0.85	9.6

Temperature: 35 °C; Pressure : 50 psig

<sup>1</sup> Vu, D. Q.; Koros, W. J.; Miller, S. J., "Mixed Matrix Membranes Using Carbon Molecular Sieves I. Preparation and Experimental Results", *Journal of Membrane Science* **2003**, 211, 311-334.

<sup>2</sup> Breck, D. W. *Zeolite Molecular Sieves: Structure, Chemistry, and Use*; John Wiley & Sons: New York, **1974**.

### RTI

Pure-gas permeation data collected last month on membrane standards in the modified high-pressure membrane permeation system at RTI were analyzed and indicated that the system was not operating satisfactorily. Two polymer membrane standards had been used: a poly(dimethylsiloxane)

membrane and a much lower-permeability polycarbonate film. For both membranes, the system gave fluxes and selectivities that were much lower (by 30-40%) than the known values, which had easily been obtained before on the same (or similar) samples by the same permeation method. This difference between measured and known values is outside the experimental error range typically seen on this system in the past. We are currently troubleshooting the system to determine the reason for this behavior and suspect a subtle leak in a system line or from the permeation cell. A fully operational system is anticipated by next month.

Due to the temporary system validation issues discussed above, permeation testing of the tubular PBI composite membrane module purchased from Pall Corporation has been rescheduled to start next month. This PBI membrane module will be evaluated with pure gases to check its integrity and, if defect-free, with a three-component syngas mixture. The PBI composite membrane module will be a good initial step toward demonstrating the proposed thin-film composite (multilayer) membrane approach as one method to increase the flux of high-temperature polymer membrane materials into a range suitable for commercial deployment.

***TASK 3: Evaluate Membrane Reactor Properties***

RTI

This task is not yet scheduled to begin at RTI.

***TASK 4: Characterize Thermal and Morphological Properties of Membranes***

UT

No significant activities occurred for this task at UT during this report period.

RTI

No significant activities occurred for this task at RTI during this report period.

***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 third monthly project report was prepared.

## Section II: Problems/Solutions

<p><b>Problem(s) Identified</b></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 problems were encountered this period.</p> <p><u>RTI</u></p> <p>Two issues were encountered this period: (i) Dissolving the Celazole grade of PBI in known solvents (e.g., DMAc) for this thermally stable polymer was more difficult than expected at room temperature and at temperatures near boiling point of water. However, project progress should be minimally affected because we anticipate that more aggressive dissolution temperatures (i.e., elevated temperatures of 150-260 °C) will solve this issue. (ii) The high-pressure membrane permeation apparatus gave flux and selectivity data that are unacceptably lower than the known values for the membrane standards tested. This difference is not within the expected experimental error range for the permeation system. The system issue has delayed the start of the PBI membrane module testing by about a month.</p>
<p><b>Proposed Solution(s)</b></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>(i) The Celazole PBI should fully dissolve in DMAc solvent if much higher temperatures (150-260 °C) are used. We saw this month that even raising the temperature to only 95 °C resulted in significant PBI dissolution in DMAc. (ii) Inaccurate calibration factors for the gas chromatograph (GC) could be a possible cause for the permeation system issue; however, the GC has been found to be satisfactory after several rechecks. Rather, we suspect that the permeation system issue is most probably related to a subtle leak in a system line or from the permeation cell.</p>
<p><b>Action(s) Conducted and Results</b></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>(i) To reach the proposed higher temperatures for dissolving PBI in DMAc, one method is to use a hot silicone oil bath. High-temperature silicone oil bath fluid, glass beakers, and higher-range thermometers were thus ordered so that higher dissolution temperatures of 150-260 °C can be tried next month. (ii) The permeation system is still undergoing troubleshooting to determine why permeation data could not be obtained with acceptable accuracy after its reconfiguration. GC calibration and operation were rechecked and deemed</p>

satisfactory. Small subtle leaks and any other problems were (will be) corrected as soon as they were (are) found. We will continue to use the polymer membrane standards mentioned in Section I to guide the troubleshooting.

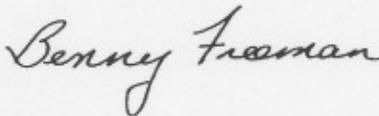
**Section III. Goals and Issues for Succeeding Period:** *(Please provide a brief description of the goal(s) you hope to realize in the coming period and identify any notable challenges that can be foreseen)*

UT

The following experiments will be conducted during the month of May 2005. A study of the effect of SiO<sub>2</sub> loading on Ultem-1000-based nanocomposite permeability will be conducted with particles loadings of 5, 10, and 15 vol%. The gases to be tested will include CO<sub>2</sub>, H<sub>2</sub>, O<sub>2</sub>, N<sub>2</sub>, and CH<sub>4</sub>. Samples of each material will be sent to RTI for high-temperature gas transport testing. Various physical and thermal properties will be characterized for these materials. If time permits, SiO<sub>2</sub>-filled Matrimid will be prepared and characterized in the same manner as the SiO<sub>2</sub>-filled Ultem 1000.

RTI

Next period, we plan to complete troubleshooting of the membrane permeation system to ensure that it is giving accurate data. Once the system is running properly, the PBI composite membrane module will be tested with a ternary syngas mixture of H<sub>2</sub>, CO<sub>2</sub>, and CO as a function of feed pressure and temperature (up to 250-300 °C). Much higher temperatures (>150 °C) will also be used in another attempt to make fully dissolved 10-15 wt% Celazole PBI solutions in DMAc. The resulting solutions will be cast into PBI membrane films, which, if good, will be evaluated for their gas separation properties. Additionally, thermogravimetric analysis (TGA) studies on Celazole PBI and the nanocomposite membrane samples to be received from UT will start next month to characterize their thermal stability (Project Task 4).



\_\_\_\_\_  
Authorized Project Representative's Signature

Date: May 11, 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.*