

NTRD Program Disclaimers

1. Disclaimer of Endorsement:

The posting herein of progress reports and final reports provided to TCEQ by its NTRD Grant Agreement recipients does not necessarily constitute or imply an endorsement, recommendation, or favoring by TCEQ or the State of Texas. The views and opinions expressed in said reports do not necessarily state or reflect those of TCEQ or the State of Texas, and shall not be used for advertising or product endorsement purposes.

2. Disclaimer of Liability:

The posting herein of progress reports and final reports provided to TCEQ by its NTRD Grant Agreement recipients does not constitute by TCEQ or the State of Texas the making of any warranty, express or implied, including the warranties of merchantability and fitness for a particular purpose, and such entities do not assume any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represent that its use would not infringe privately owned rights.

**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: July 1, 2005

Ending Date: July 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 Preparation: Preparation of more homogeneous Ultem[®] 1000 polyetherimide (PEI) nanocomposite membranes filled with 20-nm, metallic Ni nanoparticles continued. Several methods (e.g., ultrasonication versus stirring by magnetic stirring rod) for uniformly dispersing Ni particles in Ultem polymer casting solutions were tried. Additionally, it was found that Ni particles do not remain dispersed in the polymer solution (especially the ultrasonicated solution) but tend to settle out quickly to the bottom of the solution. Stabilization of particle dispersion by increasing the polymer solution viscosity will therefore be investigated within the next month or two. At present, our preferred method for making Ni/Ultem blend membranes is by vigorous shaking followed by immediate casting of Ni-loaded Ultem solutions into membrane films. Developing good methods for dispersing metal nanoparticles in polymer nanocomposite membranes is important because it will result in more homogeneous membranes with better reproducibility and characterization of gas permeation, thermal, and mechanical properties. If nanoparticle dispersion is poor, final particle concentration in the resulting membranes would be very non-reproducible and difficult to control from batch to batch, making it

also difficult to understand the impact of nanoparticle addition on base polymer properties. **(Project Task 1)**

- **High-Temperature Gas Permeation System:** Further consideration of the design of the high-temperature gas permeation system proposed last month resulted in a small design modification this period. To prevent and minimize leaks and potential safety problems, the connection joints in the permeation system to be constructed at UT will be welded rather than connected with VCR fittings. A suitable welding facility and the appropriate parts needed are currently being determined and selected. Construction of this system is important because it will allow for high-temperature, pure-gas permeation characterization of membranes in this project, as called for in the original proposal **(Project Task 2)**

RTI

- **PBI Membrane Preparation:** More free-standing, pure polybenzimidazole (PBI) and PBI/silica nanocomposites membranes continued to be prepared for permeation and thermal property testing. Because the thin (6- to 8- μm -thick), pure PBI films made earlier by knife-casting were found to be defective, thicker PBI films were made by casting into glass rings. Two PBI membranes with film thicknesses of about 20 and 34 μm were prepared in this manner and are ready for permeation testing.

A new batch of 14 wt% PBI casting solutions containing 5, 10, and 30 wt% 10-nm SiO_2 nanoparticles were made and are being cast into nanocomposite membranes. Because of fragility problems encountered with the preliminary 30 wt% SiO_2 /PBI membranes made last month, the 30 wt% SiO_2 /polymer solution mixture was drawn onto glass plates using different casting-knife gaps to check whether final film strength is affected by drawn film thickness. Unfortunately, the resulting PBI+30 wt% SiO_2 nanocomposite films were still too brittle to test their permeability. Thus, we will focus more on preparing future PBI nanocomposites with SiO_2 loadings much less than 30 wt%.

From last month's thermogravimetric analysis (TGA) results, complete removal of solvent and/or moisture from PBI-based membranes was more difficult than expected. The presence of this solvent/moisture could significantly influence membrane permeation properties. Thus, the effect of post-heat-treating the PBI-based membranes at 250 °C for 18-24 h under N_2 is also being examined. After post-heat treatment, these membranes will be tested by TGA to determine whether complete removal of residual solvent/moisture has been achieved.

Additionally, we resumed attempts to make PBI composite (multilayered) membranes on microporous substrates. Trial coatings of a PBI solution were made onto a Mott Corporation 316L stainless steel support with 0.5- μm pore size to determine whether this substrate type is a viable option to use for PBI composite membranes.

Making reproducible, defect-free PBI membranes as dense films with and without nanofillers and as thin-film composite membranes is a very important step in the development of useful gas separation membranes for this project. **(Project Task 1)**

- **Membrane Permeation Testing:** With the gas chromatograph (GC) repaired and recalibrated last month, final validation of the combined membrane permeation—GC system was completed using two membrane standards. The system validation demonstrated that the system is now operating properly and giving accurate gas permeation data on membranes tested.

Permeation-testing of pure PBI films with pure gases was therefore begun this month. Several thin (6- to 8- μm -thick), knife-cast PBI membranes tested were found to be defective. A roughly 20- μm -thick PBI film is currently being tested and appears to be defect-free thus far. Characterization of the neat (unfilled) PBI permeation properties is important because very little permeability information is available in the literature for this high-temperature-resistant,

low-permeability polymer. The gas transport data for pure PBI is also important as they will be the base values to which the permeation data for PBI nanocomposites will be compared to understand the effect of nanofiller addition. (*Project Task 2*)

- Thermal Property Characterization: TGA studies continued on some of the filled and unfilled PBI and Ultem 1000 PEI samples. Last month, we speculated that the 5-20% TGA weight loss observed in the stages before the onset of rapid thermal decomposition in these samples was due to loss of sorbed moisture and residual solvent rather than to loss of actual polymer. To confirm this moisture/solvent loss, the single-scan TGA procedure used last month was modified by including an initial TGA scan (#1) with isothermal hold step(s) that was (were) held for 30 min at one or two intermediate temperatures before cooling the samples to room temperature. Immediately following this Scan #1, the samples were then heated to 750 or 800 °C in Scan #2 to complete this "dual-scan" TGA test.

The "dual-scan" TGA test protocol was completed in an inert helium atmosphere on (i) pure PBI film and PBI nanocomposites doped with 10 and 30 wt% SiO₂ and (ii) pure Ultem 1000 film and Ultem 1000 nanocomposites filled with 10 and 20 vol% SiO₂. The new TGA data show that no intermediate material degradation (as evidenced by weight loss) occurs at temperatures below the well-defined thermal decomposition temperature of 572-575 °C for PBI-based films and 510-519 °C for Ultem-based membranes. This result supports our hypothesis of residual moisture/solvent removal from the membranes at intermediate high temperatures. The TGA studies are important for determining thermal stability (and, hence, applicability) of the neat polymer membranes and polymer-based nanocomposite membranes being developed for the targeted elevated-temperature range for gas separation. (*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

Preparation of homogeneous Ultem[®] 1000 nanocomposite membranes filled with 20-nm Ni nanoparticles continued. Because dispersion of Ni particles in membrane casting solutions of Ultem 1000 in chloroform was not as straightforward as anticipated, several different dispersion techniques, including stirring by magnetic stirring rod, ultrasonication, and vigorous shaking, were tried. Currently, our preferred preparation method giving the most uniform dispersion of Ni particles is to mechanically mix the particles into Ultem solutions by vigorous shaking followed by immediate casting of the Ni-doped Ultem solutions into membranes. This method provides more homogenous Ni-filled membranes than either ultrasonication or mixing via magnetic stirring rod. Other forms of mechanical mixing (i.e., with a high-speed blender) to uniformly disperse the filler in polymer solutions are still being investigated.

Another significant observation is that the Ni particles appeared to fall quickly out of the Ultem polymer casting solution, particularly the ultrasonicated polymer/particle mixture, before a membrane could be cast. A majority of the Ni particles were thus left behind in the mixing vessel rather than in the membrane film cast on the casting plate. To better stabilize the particle dispersion once the Ni has been mixed into the polymer solution, we will try to increase the viscosity of the host Ultem/chloroform solution, for example, by raising the polymer concentration. The higher polymer solution viscosity should alleviate or, at least, minimize filler particle sedimentation.

RTI

More polybenzimidazole [PBI] membranes, both filled and unfilled with silica nanoparticles, continued to be prepared for permeation and thermal stability testing. Because the thin (6- to 8- μm -thick), pure Celazole[®] PBI films initially made by knife-casting were found to have defects (i.e., pinholes) during permeation tests, thicker Celazole PBI films were formed by solution-casting into glass rings supported on glass plates. Though earlier thick PBI films had been too brittle for permeation tests, we could now prepare more robust PBI membranes after several attempts at making them under various film casting and drying conditions. A neat PBI film with a thickness of roughly 20 μm was made successfully and is being evaluated in permeation tests. Pure PBI films were also prepared from an unspecified grade obtained from Pall Corporation. A dense, 34- μm -thick Pall PBI membrane is ready and will be permeation-tested after testing of the 20- μm sample is completed. For a better comparison between the Celazole and Pall grades, a thinner Pall PBI film closer to the 20- μm thickness of the Celazole film is also being made.

For PBI nanocomposite membranes, a new batch of 14 wt% Celazole casting solutions containing different loadings of Aldrich 10-nm SiO_2 nanoparticles were made using the procedure described last month. In addition to the 10 and 30 wt% concentrations still being studied, a solution mixture with a lower 5 wt% SiO_2 content was prepared to provide an additional data point for investigating the effect of nanofiller content on gas separation properties of PBI/ SiO_2 nanocomposite membranes.

Because initial knife-cast PBI membranes filled with 30 wt% SiO_2 were very brittle (cf. previous monthly report), different casting-knife gaps were used this period to prepare additional PBI+30 wt% SiO_2 nanocomposites, to determine whether film thickness affects film robustness. After drying for 24 h at 70 °C under N_2 , the resulting PBI+30 wt% SiO_2 blend films were still too brittle to test their permeability. Thus, we will focus on preparing future PBI nanocomposites with SiO_2 loadings much less than 30 wt%.

Effect of a high-temperature post-heat treatment step on the properties of PBI-based membranes is also currently being investigated. Results from last month's thermogravimetric analysis (TGA) studies indicated that drying PBI-based films at 70-100 °C for 1-4 days appears to be insufficient for completely removing solvent and moisture. The presence of leftover solvent/moisture could have a significant effect on membrane permeability. Thus, for some newly cast filled and unfilled PBI films, they were placed back into the oven at 250 °C for 18-24 h under N_2 purge after the film drying step (i.e., 70 °C for 24 h under N_2) and their removal from the glass casting plates. These membranes will be tested by TGA to determine whether complete residual solvent/moisture is achieved by the 250 °C post-heat treatment.

Trial preparation of PBI composite membranes is also currently being reattempted by coating the 14 wt% PBI solution in DMAc (*N,N*-dimethylacetamide) onto a microporous, 316L stainless steel support substrate with 0.5- μm pore size from Mott Corporation. If a good composite membrane can be obtained, then we will acquire microporous steel substrates of a more suitable size and form (i.e., thinner and in disk form) for our existing permeation setup.

TASK 2: Evaluate Membrane Permeation Properties

UT

For the proposed high-temperature gas permeation system to be built at UT for pure-gas permeation characterization of membranes in this project, a small modification to the original system design was made. To prevent and minimize leaks and potential safety problems, the connection joints in the permeation system will be welded rather than connected with VCR fittings. A suitable welding facility and the appropriate parts needed are currently being determined and selected. Next period, parts and equipment will be ordered, and construction of the high-temperature permeation system will commence.

RTI

With the on-line gas chromatograph (GC) analytical system repaired last month, final validation of the combined membrane permeation—GC system was completed using two membrane standards with known gas permeation properties. Pure-gas permeabilities and selectivities measured on the membrane standards were consistent with the known values, indicating that the repaired GC—permeation apparatus is now operating properly.

Several 6- to 8- μm -thick, knife-cast PBI film samples were loaded into the permeation cell and tested with pure gases at room temperature. These thin, knife-cast membrane films were found to be defective mainly due to pinholes; thus, they were not able to hold pressure and had very high permeate flow rates.

A thicker PBI film (~20 μm in thickness; Celazole grade) is currently being tested with pure H_2 and CO_2 and, thus far, seems to be defect-free, displaying very low permeability at 23 °C. If its pure-gas permeation properties are good, the film will be tested with a syngas mixture at room temperature before proceeding to a temperature dependence study. When testing of this film is done, a 34- μm -thick PBI film made from the Pall polymer grade will be evaluated in a similar fashion.

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 period.

RTI

Thermogravimetric analysis (TGA) studies in an inert helium environment continued on the following six membrane samples by using a "dual-scan" TGA protocol rather than the single-scan program used last month:

- Pure PBI film
- Pure Ultem 1000 PEI film
- PBI films filled with 10 and 30 wt% Aldrich 10-nm SiO_2
- Ultem 1000 PEI films loaded with 10 and 20 vol% Aldrich 10-nm SiO_2

All samples were cut from the remaining host films used previously for TGA. For the pure PBI sample specifically, it was obtained from Celazole Sample #3. All Ultem-based samples had been made by UT.

In last month's single-scan TGA results (cf. June 2005 status report), initial stages of weight loss were observed before the onset of rapid thermal decomposition in the PBI- and Ultem-based membranes. The PBI-based films had displayed two early weight-loss stages: (i) Stage 1 loss of about 12-13% as temperature rose to 180 °C and (ii) Stage 2 loss of an additional 3-7% relative to that in Stage 1, starting at 260-270 °C and leveling off around 430-480 °C. The Ultem-based films had shown one early weight-loss stage of 5-9% as temperature increased to 360-375 °C. These losses in sample weight had been speculated to be losses of (i) sorbed moisture on the sample surface and bound inside the PBI or

Ultem matrices and/or (ii) residual solvent bound inside these solvent-cast membranes, rather than to loss of actual polymer mass.

To verify the moisture/solvent loss hypothesis, a "dual-scan" TGA procedure made up of two sequential temperature programs was used. In TGA Scan #1, to facilitate removal of moisture/solvent, membrane samples were heated to and then held isothermally for a given runtime period at intermediate high temperature(s). In the case of PBI-based films, Scan #1 heated from room temperature to 130 °C, held at 130 °C for 30 min, then heated from 130 °C to 400 °C, held at 400 °C for 30 min, and finally cooled to room temperature. For Ultem-based samples, Scan #1 heated from room temperature to 250 °C, held at 250 °C for 30 min, and then cooled to room temperature. The subsequent TGA Scan #2 heated samples from room temperature to 800 °C (PBI-based films) or 750 °C (Ultem-based films) and held them at this final temperature for 30 min. All TGA scans done during this period were performed in helium.

The dual-scan TGA results are presented in Figures 1 and 2 for the PBI- and Ultem-based samples, respectively. Scan #1 accurately replicates the early weight-loss stages observed in last month's single-scan TGA data. When Scan #2 is performed, no other weight losses appear until the onset of rapid thermal decomposition. Thus, the dual-scan TGA data demonstrates that Scan #1 aided the removal of sorbed moisture and residual solvent from the samples. If weight loss at intermediate temperatures were instead due to polymer degradation, then it would have been evident again during Scan #2; however, this was clearly not the case. The entire Scan #2 weight loss profile stays stable (constant) until the decomposition onset temperature.

TGA Scan #2 is thus a truer representation of the thermal stability behavior of the membrane samples. A direct comparison of the Scan #2 data of the base polymers and their silica-filled nanocomposites is shown in Figure 3. The percentage weight loss values in these plots have been adjusted by referencing back to the starting Scan #2 weights of the sample. Decomposition onset temperatures are identical to those obtained by the single-scan TGA method (cf. June 2005 report): 572-575 °C for PBI-based films and 510-519 °C for Ultem-based membranes. As seen last month, addition of nanosilica particles does not seem to have a clear positive or negative effect on thermal stability of the base PBI polymer (Fig. 3a). Incorporation of silica, though, still slightly increases thermal degradation temperature (i.e., thermal stability) of the base Ultem 1000 matrix by 8-9 °C (Fig. 3b).

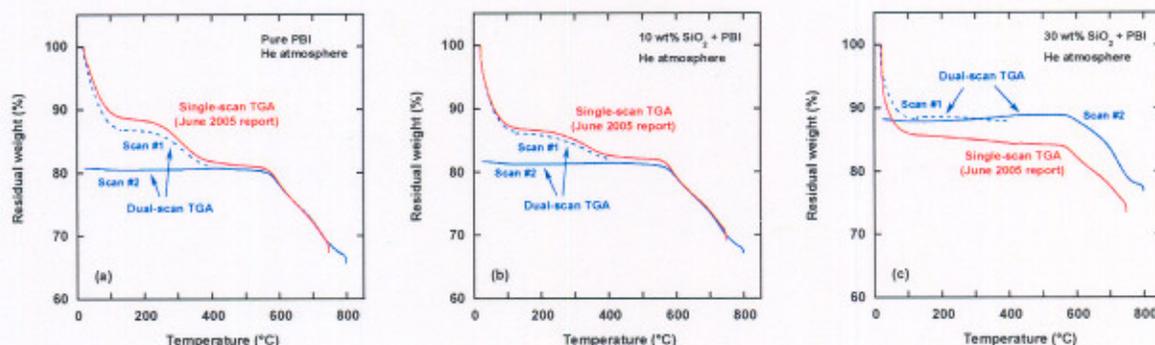


Figure 1. Weight loss curves obtained using dual-scan TGA test protocol described in this report for (a) pure PBI film and nanocomposite films of (b) 10 wt% SiO₂ + PBI and (c) 30 wt% SiO₂ + PBI. All TGA scans were done in He at 10 °C/min heating rate. Initial sample weights: 3.09673 mg for pure PBI; 2.62225 mg for 10 wt% SiO₂; and 1.30348 mg for 30 wt% SiO₂. Aldrich SiO₂ nanoparticles having a 10-nm primary particle diameter were used in the nanocomposites. Corresponding single-scan TGA curves from the June 2005 monthly report are also included in the plots for comparison.

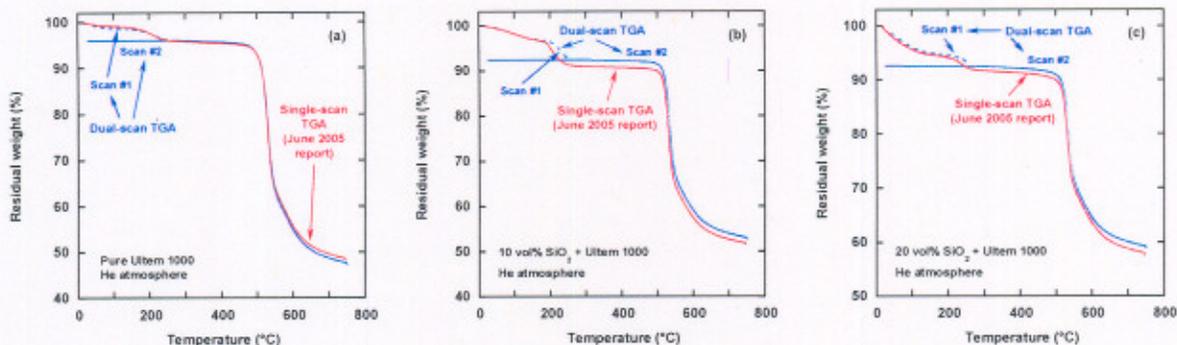


Figure 2. Weight loss profiles obtained with dual-scan TGA test protocol described in this report for (a) pure Ultem 1000 PEI film and nanocomposite films of (b) 10 vol% SiO₂ + Ultem 1000 and (c) 20 vol% SiO₂ + Ultem 1000. All TGA scans were conducted in He at 10 °C/min heating rate. Initial sample weights: 15.4375 mg for pure Ultem 1000; 21.8747 mg for 10 vol% SiO₂; and 22.2811 mg for 20 vol% SiO₂. Aldrich SiO₂ nanoparticles having a 10-nm primary particle diameter were used in the nanocomposites. Corresponding single-scan TGA curves from the June 2005 monthly report are also included in the plots for comparison.

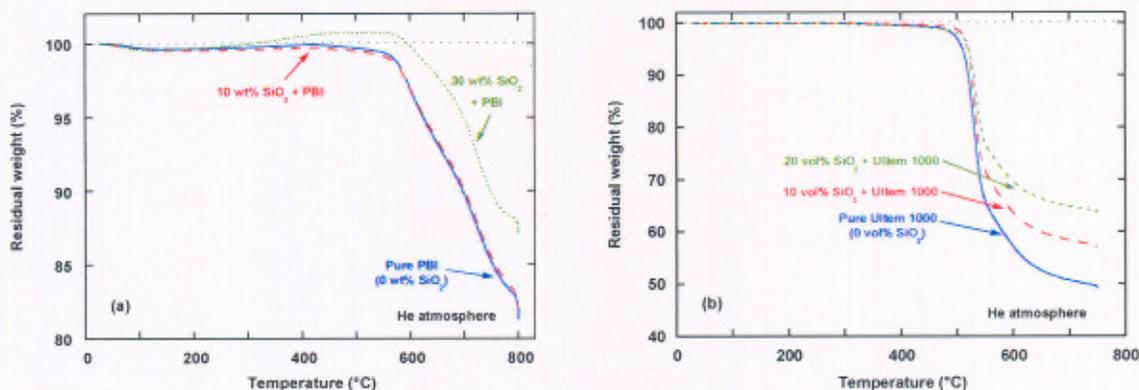


Figure 3. Comparison of TGA Scan #2 weight loss profiles for (a) PBI nanocomposites and (b) Ultem 1000 PEI nanocomposites, both filled with different concentrations of Aldrich 10-nm SiO₂ nanoparticles. Obtained in He at 10 °C/min heating rate according to dual-scan TGA protocol described in this report, data plotted have been referenced back to starting Scan #2 sample weights. Starting Scan #2 sample weights: (a) 2.50172 mg for pure PBI; 2.14229 mg for 10 wt% SiO₂; and 1.15019 mg for 30 wt% SiO₂ and (b) 14.8337 mg for pure Ultem 1000; 20.2200 mg for 10 vol% SiO₂; and 20.6433 mg for 20 vol% SiO₂.

A clearer, revised comparison of the thermal stability behavior of pure PBI and pure Ultem 1000 PEI is made in Figure 4, which was created from TGA Scan #2 data collected this period. The true thermal behavior of the polymers was somewhat less clear when the comparison was made using the single-scan TGA data (cf. Fig. 4 in June 2005 report) because of the presence of the various stages of early weight loss due to residual moisture/solvent evaporation. Regardless of which data set is used, though, the conclusion is the same: PBI ($T_d \sim 572$ °C) exhibits a higher decomposition onset temperature than Ultem 1000 ($T_d \sim 510$ °C). From a thermal stability viewpoint, both of these T_d 's make PBI and Ultem potentially viable membrane (or membrane matrix) materials for the high-temperature gas separation application in this project.

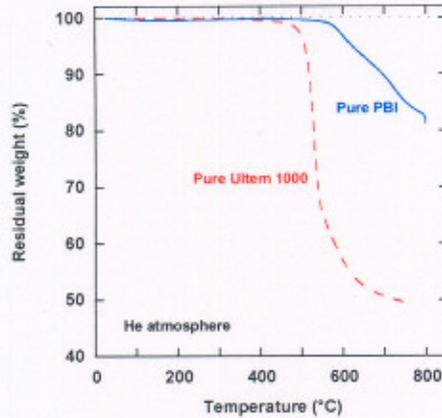


Figure 4. TGA Scan #2 curves for pure PBI and pure Ultem 1000 PEI. Acquired in He at 10 °C/min heating rate according to dual-scan TGA protocol described in this report, data plotted have been referenced back to starting Scan #2 sample weights (cf. Fig.3 caption). This plot is a revised comparison of the thermal stability behavior shown for these two polymers in Fig. 4 of June 2005 status report.

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 sixth 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 August, we plan to resolve the difficulty of Ni nanoparticle dispersion in Ultem 1000 casting solutions, test the pure-gas permeation properties of the Ni/Ultem nanocomposite membranes that have already been made, and conduct DSC on Ultem-based nanocomposites. We will also finish ordering the parts needed for the high-temperature permeation system to be built at UT and begin its construction once these parts are received.

RTI

Next period, we will continue to evaluate the intrinsic permeation properties of the 20- μm -thick Celazole PBI film and the 34- μm -thick Pall PBI film as long as they stay defect-free. Testing will then start on the tubular PBI composite membrane module. If time permits, permeation-testing will also start on PBI nanocomposite membranes. Preparation of PBI and PBI nanocomposite films will continue by ongoing optimization of the membrane casting and drying procedures. In particular, on the basis of this month's TGA results, future PBI-derived membranes should be dried at higher temperatures and/or longer times because of the measurable amount of residual solvent/moisture apparently left in them. Additionally, attempts will continue to prepare thin-film PBI composite membranes on microporous stainless steel support substrates from Mott Corporation.

Thermal stability of the PBI, Ultem 1000 PEI, and their nanocomposite membranes will be determined by TGA in a *syngas mixture* environment containing H_2 , CO and CO_2 to provide a more

realistic evaluation of material performance under conditions closer to those of the actual application. TGA experiments will also be performed on PBI-based membranes that have undergone a 250 °C post-heat treatment step for 18-24 h under N₂ to gauge whether this heat treatment achieves complete removal of residual solvent/moisture from the membranes.

Benny Freeman

Date: September 26, 2005

Authorized Project Representative's Signature

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.*