

## **NIRT: Fabrication of hollow fiber polymer/porous-layer nanocomposite membranes for gas separations**

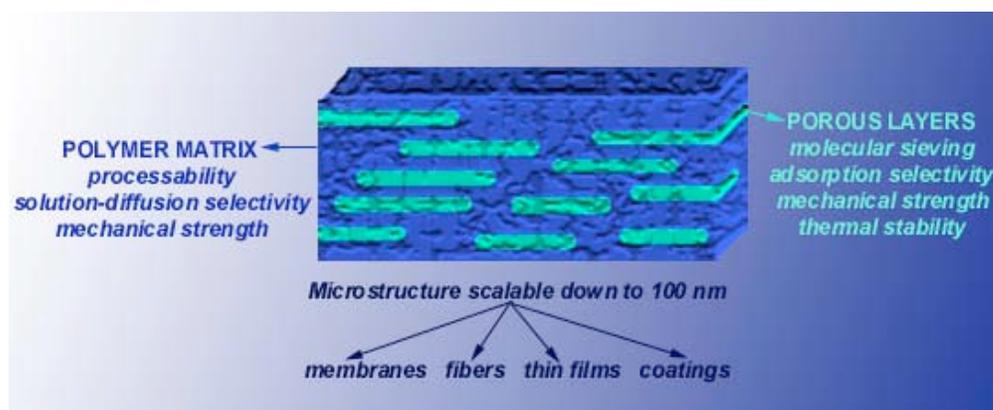
*NSF NIRT Grant NSF/CTS-0403574*

*PIs: Michael Tsapatsis ([tsapatsi@cems.umn.edu](mailto:tsapatsi@cems.umn.edu)), Frank S Bates, William J Koros, Eva Marand, Sankar Nair, Associate Member: Efrosini Kokkoli*

*University of Minnesota, Georgia Institute of Technology, Virginia Polytechnic Institute  
Collaborations: NIST, Pall Corp., Science CentrUM*

*Web site: <http://www.cems.umn.edu/research/tsapatsis/NIRT/index.htm>*

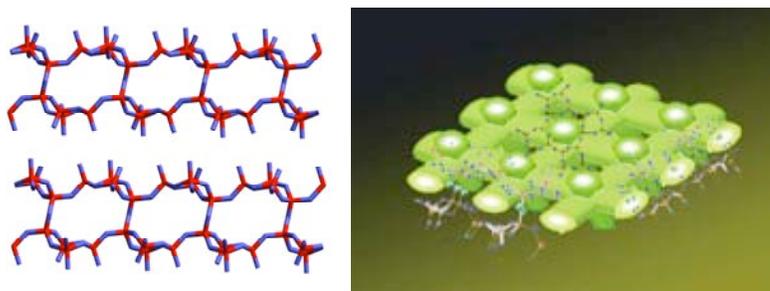
**Introduction:** The potential economic and environmental benefits of low cost, reliable membrane technology in the chemical process industry and smaller volume distributed applications are well established. In addition to energy savings, membrane technology may allow novel chemical processes and energy production devices that eliminate by-product formation at the source. A major class of important separations is that of gas separations by membranes. Currently, it is dominated by polymeric materials that can be produced as hollow fibers with thin (100nm) permselective skins. However, despite the ability to produce robust membranes at large quantities and relatively low cost, wider implementation of this technology is hindered by intrinsic permeability and selectivity limitations of the polymeric materials it currently employs. This interdisciplinary research team works towards the development of a new nanostructured membrane technology that overcomes current limitations. We combine novel nanometer-thick selective porous inorganic layers with existing and newly synthesized polymeric matrices employing appropriate synthetic and processing technologies (Figure 1). The ultimate goal is to design and fabricate materials with superior permeability properties that are amenable to large scale production as thin skin asymmetric hollow fibers and sheets.



**Figure 1.** The concept of *polymer/ microporous-layer nanocomposite*: introduction of *selective flakes* in *mixed matrix composites*. The thickness of the porous layers is from 1-10nm and therefore, the composite can in principle be scaled down to 100nm thick films preserving its properties.

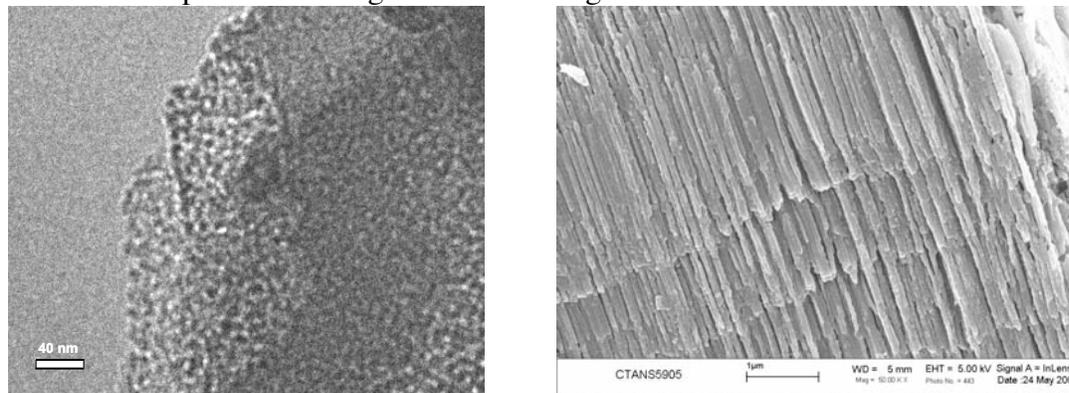
**Current Status:** Seven PhD graduate students are working in this project. Six are supported directly by the NIRT funding and one by a NSF fellowship. Good communication between the groups has been established and well documented film casting and testing procedures have been developed and reproduced at the three Universities.

To be used as additives, we are investigating various inorganic materials (including layered silicates and aluminophosphates). As examples, we mention here a material called AMH-3 and a layered aluminophosphate. The former is the first layered silicate with pores larger than 3 Angstroms perpendicular to the layer (Figure 2), while the latter is a layered material containing aluminophosphate nets (4x6x8-member-ring nets) with small pores perpendicular to the layers. We have been able to prepare symmetric planar composites of these materials with polymer matrices and we are currently evaluating microstructure and permeation properties. In parallel, we developed simulations to predict transport through nanocomposites of AMH-3 layers with polymer matrices. Finally, we are making progress in being able to manufacture polymer-silicate nanocomposites as asymmetric hollow fibers.



**Figure 2.** The crystal structure of the silicate layers (silicon=red; oxygen=blue) of AMH-3 (left). Schematic of the three-dimensional layer pore structure of AMH-3 (right). Tsapatsis Group *UMN*.

*Fabrication and Testing of Nanocomposites:* We synthesized several layered aluminophosphates and the layered silicate AMH-3. We developed swelling and delamination procedures for these layered materials and we characterized the resulting materials by Transmission and Scanning Electron Microscopy (Figure 3), X-Ray Diffraction and Small Angle X-Ray Scattering. Recently, we developed ion exchange exfoliation procedures for AMH-3 that allowed us to fabricate composites with high silicate loadings.

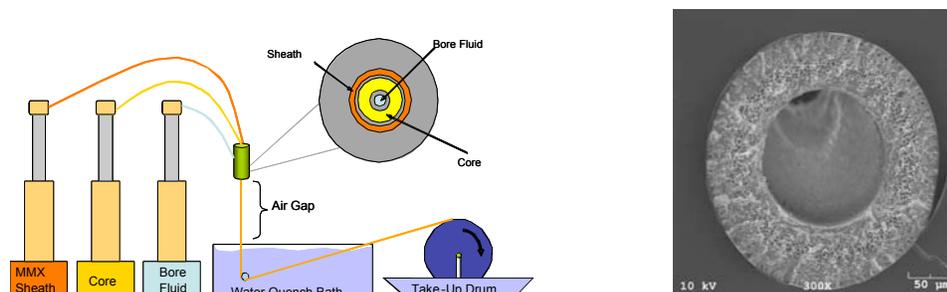


**Figure 3:** Transmission Electron Microscopy image of exfoliated AMH-3 (left) and Scanning Electron Microscopy image of surfactant swollen aluminophosphate (right). Tsapatsis Group *UMN* and Marand Group *VPI*.

*Modeling Transport through Nanocomposites:* Our simulations aim at predicting the molecular transport of gas molecules in nanocomposite films. Poly(dimethylsiloxane) (PDMS) and the layered silicate AMH-3 were first used as model polymeric and porous layered materials for

studying the diffusion of small gases ( $H_2$ , He,  $N_2$  and  $O_2$ ) in nanocomposites with varying inorganic loadings of AMH-3. Diffusion data obtained from molecular transport through polymeric membranes were compared with experimental values to validate some of the predictions. The diffusivity increases with decrease in penetrant size in both membranes, in agreement with the literature data. The diffusion of molecules (He,  $H_2$ ,  $O_2$ ) is predicted to be faster in the composite membrane than the polymeric membrane. This is due to presence of porous AMH-3 layer in the composite. The  $H_2/N_2$  selectivity in the composite membrane is found to be enhanced over that in the pure PDMS membrane (15 vs. 4). We also found a small  $O_2/N_2$  selectivity in the composite membrane as opposed to no selectivity in pure PDMS.

**Hollow Fiber Spinning:** We performed spinning trials (Figure 4) using Ultem® as the polymer and Laponite® RD as the particulate. Although Laponite® RD is a dense silicate and therefore no selectivity improvement is expected, it was selected for our spinning trials since it is available in large quantities and from the processing standpoint is representative of layered silicates. Figure 5 shows an SEM of a defect-free Torlon® hollow fiber membrane. The concentricity and lack of macrovoids are typical of state of the art fiber membranes. Recently, we have successfully produced a mixed matrix hollow fiber using Ultem® as the polymer and Laponite® RD as the particulate.



**Figure 4.** Schematic of the hollow fiber spinning process (left) and Scanning Electron Microscopy image of a hollow fiber fabricated in our lab (right). Koros Group *Georgia Tech*.

**Future Work:** We will continue composite fabrication using different porous fillers and different polymers including diblock and triblock copolymers. The microstructure will be characterized by Transmission Electron Microscopy, X-Ray Diffraction and Small Angle X-Ray and Neutron Scattering. The membranes will be tested for gas separation performance. In parallel we will continue to develop fiber spinning protocols to manufacture hollow fibers with nanocomposite separating layers and we will test the hollow fibers for gas separations. Mathematical modeling will be extended to include continuum predictive models. As stated in the proposal, during the second year we will initiate the outreach activity which includes an opportunity for a team of high school teachers to participate as part of the research team, over the course of the remaining three summers.

#### References:

1. Jeong et al., *Nature Materials* **2**:(1), 53-58 (2003) *A Highly Crystalline Layered Silicate with Three-Dimensionally Microporous Layers*.
2. Jeong et al., *Chemistry of Materials* **16**:(20), 3838-3845 (2004) *Fabrication of Polymer/Selective-Flake Nanocomposite Membranes and Their Use in Gas Separation*.
3. **U.S. Patent 6,863,983 B2**, "Layered Silicate Material and Applications of Layered Silicates with Porous Layers" Tsapatsis, M., Nair, S. and Jeong HW, 2005.