DEVELOPMENT OF NANOFILLER-MODULATED POLYMERIC OXYGEN ENRICHMENT MEMBRANES FOR REDUCTION OF NITROGEN OXIDES IN COAL COMBUSTION

FINAL REPORT

SUBMITTED BY

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ACKNOWLEDGEMENT

ABSTRACT

North Carolina A&T State University in Greensboro, North Carolina, has undertaken this project to develop the knowledge and the material to improve the oxygen-enrichment polymer membrane, in order to provide high-grade oxygen-enriched streams for coal combustion and gasification applications. Both experimental and theoretical approaches were used in this project. The membranes evaluated thus far include single-walled carbon nano-tube, nano-fumed silica polydimethylsiloxane (PDMS), and zeolite-modulated polyimide membranes. To document the nanofiller-modulated polymer, molecular dynamics simulations have been conducted to calculate the theoretical oxygen molecular diffusion coefficient and nitrogen molecular coefficient inside single-walled carbon nano-tube PDMS membranes, in order to predict the effect of the nano-tubes on the gas-separation permeability.

The team has performed permeation and diffusion experiments using polymers with nano-silica particles, nano-tubes, and zeolites as fillers; studied the influence of nano-fillers on the self diffusion, free volume, glass transition, oxygen diffusion and solubility, and perm-selectivity of oxygen in polymer membranes; developed molecular models of single-walled carbon nano-tube and nano-fumed silica PDMS membranes, and zeolites-modulated polyimide membranes. This project partially supported three graduate students (two finished degrees and one transferred to other institution). This project has resulted in two journal publications and additional publications will be prepared in the near future.

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EXECUTIVE SUMMARY

The U.S. Department of Energy (DOE) is seeking to develop advanced power generation systems such as the Integrated Gasification Combined Cycle (IGCC) process using coal or other fossil fuels. In this context, NO_x emission from the combustion and gasification of coal is a serious environmental concern of global proportion. NOx emission problem can be addressed in some significant way if the combustion could be carried out in an oxygen-enrichment environment. If high-grade oxygen-enriched streams were available at low cost, as a result of development of better oxygen-selective membranes, then combustion process through industry could be made more energy efficient.

North Carolina A&T State University in Greensboro, North Carolina, has undertaken this project to develop the knowledge and the material to improve the oxygen-enrichment polymer membrane. Based on our recent work on nanofiller-modulated polymeric oxygen enrichment membranes, we proposed and performed experimental and theoretical research to develop these membrane materials to provide high-grade oxygen-enriched streams for coal combustion and gasification applications. The major objectives are:
- Research and select polymer candidates as well as functional nano-fillers.
- Experiment with the selected nano-filler-modulated polymers and document the fundamental microstructure-property relationships.
- Develop molecular simulation models for selected membranes to document the fundamental diffusion and filler-polymer interactions.

Both experimental and theoretical approaches were used in this project. The materials limitations are prominent among the existing limitations of polymer membranes. To enhance the selectivity, the use of novel polymer nanocomposite materials modulated by different nanofillers including carbon nanotubes, fumed silica, molecular sieves were explored. Different polymers were used in the research in order to learn about the nature of the selectivity. Although the mechanical properties thus the membrane life cycles may be improved with nanocomposite technology, our primary goal was to discover and develop nanofiller modulated polymer matrix that exhibits improved selectivity while preserving high permeability. To achieve high selectivity often leads to compromises in the permeability when traditional fillers are used in so-called mixed matrix membranes. The primary method of research used to develop a membrane with the required traits has been to vary the amount and type of filler, the type of polymer backbone, and the method of distribution and casting used. The results are used to develop computational models to further study and develop the technology. The membranes evaluated thus far include single-walled carbon nano-tube, nano-fumed silica polydimethylsiloxane (PDMS), and zeolite-modulated polyimide membranes.

To document the nanofiller-modulated polymer, molecular dynamics simulations have been conducted to calculate the theoretical oxygen molecular diffusion coefficient and nitrogen molecular coefficient inside single-walled carbon nano-tube PDMS membranes, in order to predict the effect of the nano-tubes on the gas-separation permeability. The separation of gas by polymer membrane is known to be by the solution-diffusion mechanism. The selectivity of the polymer gas-separation membrane is the product of the selectivity of solubility times the selectivity of diffusivity. The diffusivity of a gas molecule inside a polymer is controlled by the kinetic diameter of the gas molecule and the free volume of the polymer. The free volume of a polymer is the difference in specific volume at the temperature and at absolute zero. The free volume increases at glass transition because the chain segments are freely sliding from each other above glass transition temperature by virtue of single bond rotations. Our research focus is centered around the mechanism of glass transition in terms of its impact on polymer membrane's oxygen enrichment selectivity. We have worked with polymers whose selectivity can be manipulated by introducing abundant polymer-nanofiller interfaces leading to incite the secondary gas-separation mechanism which can ultimately affect the selectivity at above glass transition temperature.

We have accomplished the following in this project:

- Performed permeation and diffusion experiments using polymers with nano-silica particles, nano-tubes, and zeolites as fillers.
- Studied the influence of nano-fillers on the self diffusion, free volume, glass transition, oxygen diffusion and solubility, and perm-selectivity of oxygen in polymer membranes.
- Developed molecular models of single-walled carbon nano-tube and nano-fumed silica PDMS membranes, and zeolites-modulated polyimide membranes.
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1. INTRODUCTION

The U.S. Department of Energy (DOE) is seeking to develop advanced power generation systems such as the Integrated Gasification Combined Cycle (IGCC) process using coal or other fossil fuels. In this context, NO_x emission from the combustion and gasification of coal is a serious environmental concern of global proportion. NOx emission problem can be addressed in some significant way if the combustion could be carried out in an oxygen-enrichment environment. If high-grade oxygen-enriched streams were available at low cost, as a result of development of better oxygen-selective membranes, then combustion process through industry could be made more energy efficient.

North Carolina A&T State University in Greensboro, North Carolina, has undertaken this project to develop the knowledge and the material to improve the oxygen-enrichment polymer membrane. Based on our recent work on nanofiller-modulated polymeric oxygen enrichment membranes, we proposed and performed experimental and theoretical research to develop these membrane materials to provide high-grade oxygen-enriched streams for coal combustion and gasification applications.

The overall goal of this project is to further improve upon our existing technology and further optimize the nanofiller-modulated polymer formula for the oxygen-enrichment for the coal combustion and gasification applications. The major objectives are:
- Research and select polymer candidates as well as functional nano-fillers.
- Experiment with the selected nano-filler-modulated polymers and document the fundamental microstructure-property relationships.
- Develop molecular simulation models for selected membranes to document the fundamental diffusion and filler-polymer interactions.

2. EXPERIMENTAL METHODS

We developed nanofiller-modulated polymer membrane technology capable of separating O_2 from N_2. The selected membranes must be capable of producing a sufficient volume of high purity O2 at reasonable operational and capital costs. The primary method of research used to develop a membrane with the required traits has been to vary the amount and type of filler, the type of polymer backbone, and the method of distribution and casting used. The results are used to develop computational models to further study and develop the technology. The membranes evaluated thus far include single-walled carbon nano-tube, nano-fumed silica polydimethylsiloxane (PDMS), and zeolite-modulated polyimide membranes.

Permeability measurements of the flat polymer membrane films were made using a manometric (or constant volume) method. The method relies on maintaining a constant pressure of a gas penetrant on the upstream face of the membrane film and measuring the flux across the membrane film of known thickness and area on the downstream (or permeate) face. The flux or permeation rate was measured from the pressure rise from the permeating gas in a known constant downstream (permeate) volume. The pressure rise was measured and plotted by National Instrument data acquisition board and LabVIEW software and the ideal gas law is used to calculate flux. A schematic of the permeation testing apparatus is shown in Figure 1. The apparatus was showed in Figure 2. The front panel and block diagram of LabVIEW software were showed in Figure 3. and Figure 4.

The permeability or permeability coefficient of a gas is defined by the expression [1, 2]:

$$ P = \frac{1}{P_{feed}} \cdot \frac{V_d M_{gas} d}{\rho R T A} \cdot \frac{dP_d}{dt} $$

where P_{feed} is the applied upstream pressure, V_d the downstream compartment volume, M_{gas} the molecular weight of the penetrant gas at density and A the membrane area. d is the membrane thickness.

The selectivity is defined by the expression:

$$ \alpha_{A/B} = \frac{P_A}{P_B} = \left(\frac{S_A}{S_B}\right)\left(\frac{D_A}{D_B}\right) $$

where, P is the permeability, S is solubility and D is diffusion coefficient.

In our experimental setup, P_{feed} is typically 50 psi, V_d is 50 cm^3, d is 100 miron, A is 3.14(1 inch)^2 = 3.14 inch^2, M_{O2} = 32 g/mol, M_{N2} = 28 g/mol.

Permeability is often expressed in the customary unit of Barrer (1 Barrer = 10^{-10} cm^3(STP)cm/cm^2 s cmHg).

The stainless steel sintered substrate disks were purchased from Advanced Glass and Ceramics, Holden, MA. The nominal pore size of the disks is 0.2 μm. The disk was used as the mechanical support for the polymer membrane. The membrane was prepared onto the disks by spincoating (Figure 1). The use of the stainless steel disk as the substrate allowed us to use the standard filter disk holder to house the membrane for permeation test (Figure 1.). The following figures illustrate the actual experimental setup for the permeation experiment and the National Instrument data acquisition board along with its LabView software was used to record the pressure data against time.
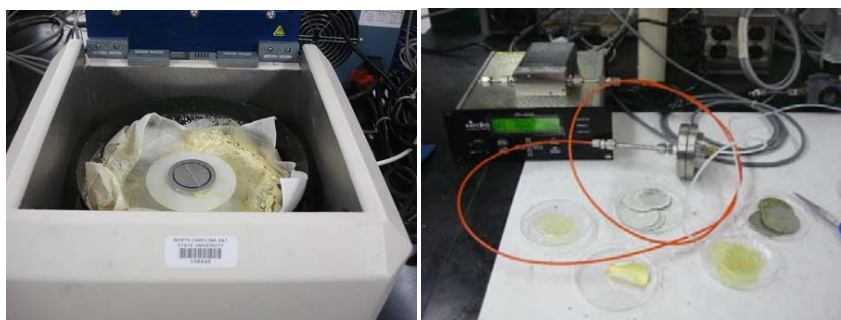
Figure 1. The spincoater (left) and the membrane holder (right) used for the preparation of the membrane and the test of the membrane.
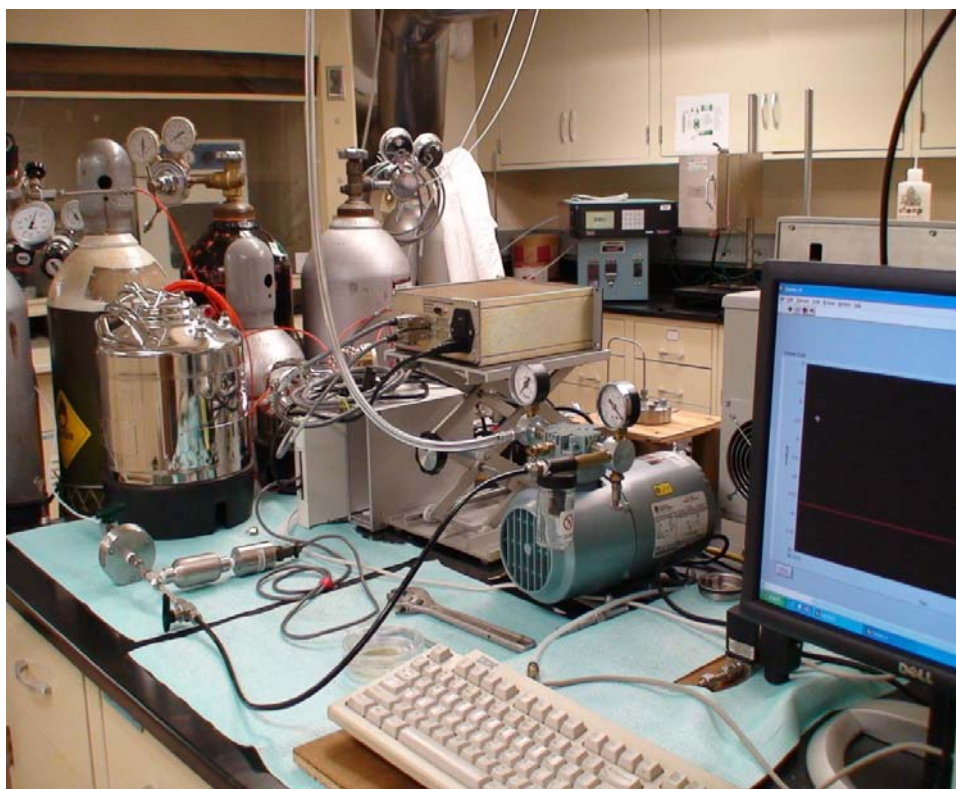

Figure 2. Experiment setup of pure gas permeation apparatus for flat membrane films.
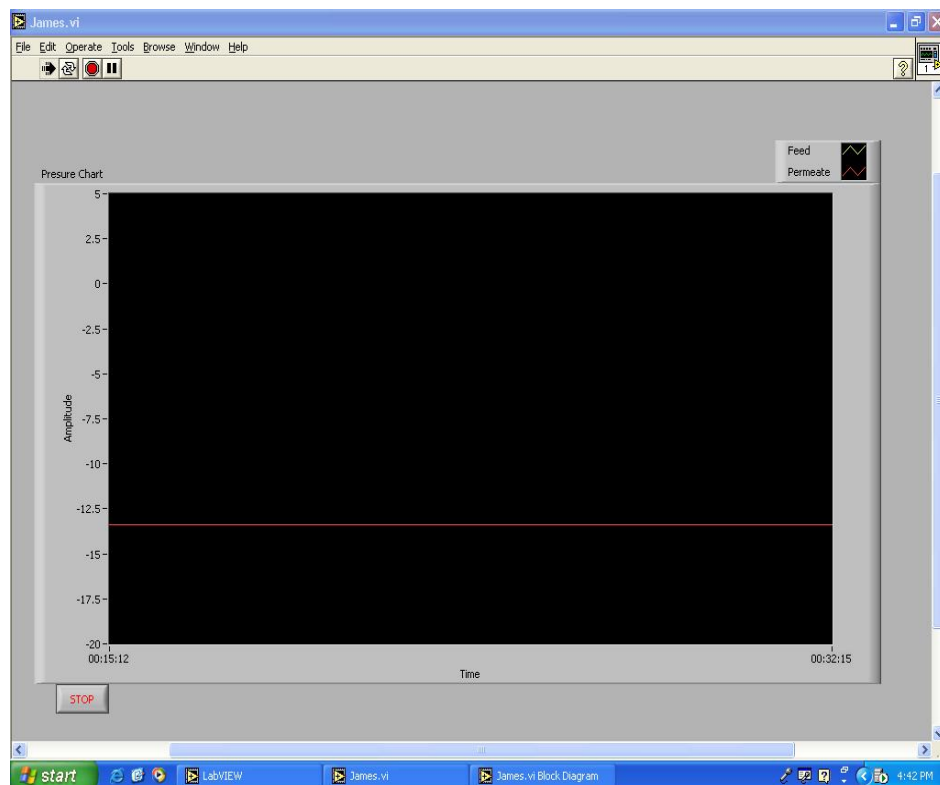
Figure 3. Front panel of LabVIEW software for the permeation testing apparatus.
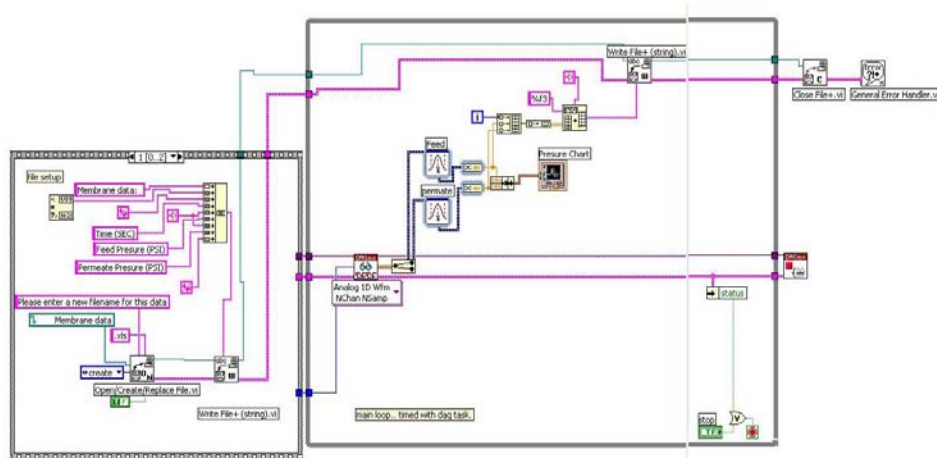

Figure 4. Block diagram of LabVIEW software for the permeation testing apparatus.

The method we used to determine the diffusion coefficient is to extract the slopes from the time-lag measurement as illustrated in Figure 5 and the steady-state permeation measurement.
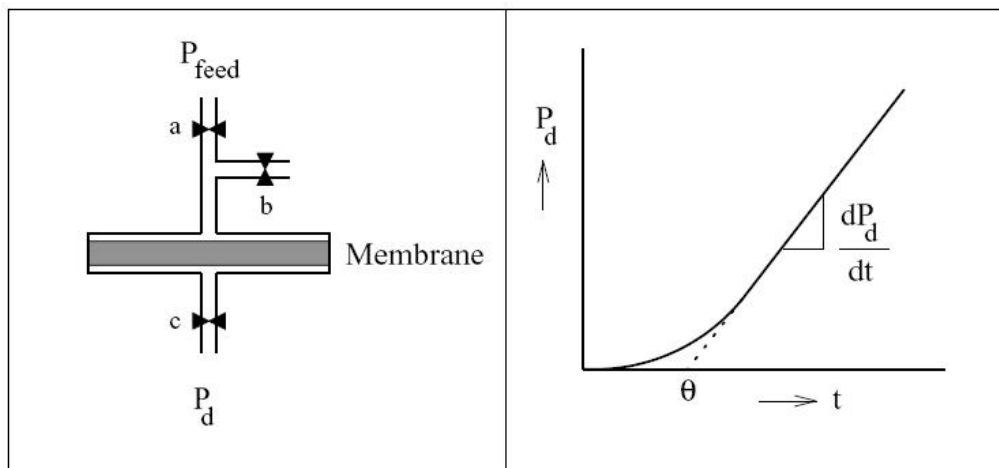

Figure 5. Left: Schematic representation of the set-up of a time-lag measurement. Before the experiment the valve (a) is closed and vacuum is applied to valves (b) and (c). Then (b) is closed and at time t = 0 valve (a) is opened and P_d is recorded. Right: A typical time-lag plot. From the time-lag the diffusion constant can be calculated directly and from the slope dP_d/dt the permeability coefficient can be calculated.

The polyimide selected was Matrimid 5218 - chosen for its high glass transition temperature, high structural and thermal stability, low cost, and high porosity. Matrimid® 5218 was bought from Huntsman Corporation and was used to prepare polymer membrane by solvent casting. Matrimid® 5218 has a high glass transition temperature (Tg) with the characteristic rigid polymer chain backbone. The chemical structure is showed in Figure 6.
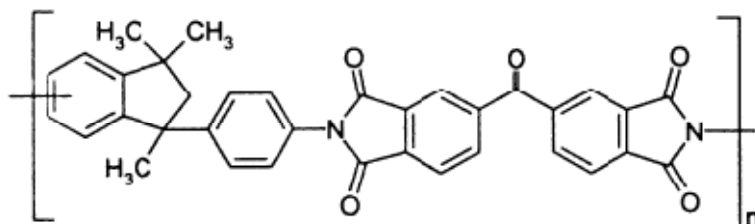

Figure 6. Chemical structures of Matrimid® 5218 polyimide from Huntsman Corp.

The polymer slurry was poured onto a flat, level, clean horizontal glass surface. A stainless steel film applicator was used to draw/spread the polymer slurry to a uniform thickness. An inverted glass funnel was also used to cover the wet film. Solvent vapor left through the small gap between the glass funnel and glass surface. The solvent from the film slowly evaporated over about a 12 h time period. The resulting dried film had an approximate thickness of about 60-100 micron. For almost all cases, the films automatically became delaminated from the glass surface during the evaporation process; so, removal was easy. Sometimes, the film remained attached to the glass surface, and it was necessary to use a razor blade and slight peeling of the film from the glass surface to initiate delamination. The final membrane film was further dried after initial evaporation at a temperature of about 100 °C for at least 12 h in a vacuum oven to remove residual solvent.

3. MOLECULAR SIMULATIONS

To document the nanofiller-modulated polymer, molecular dynamics simulations have been conducted to calculate the theoretical oxygen molecular diffusion coefficient and nitrogen molecular coefficient inside single-walled carbon nano-tube PDMS membranes, in order to predict the effect of the nano-tubes on the gas-separation permeability. The separation of gas by polymer membrane is known to be by the solution-diffusion mechanism. The selectivity of the polymer gas-separation membrane is the product of the selectivity of solubility times the selectivity of diffusivity. The diffusivity of a gas molecule inside a polymer is controlled by the kinetic diameter of the gas molecule and the free volume of the polymer. The free volume of a polymer is the difference in specific volume at the temperature and at absolute zero. The free volume increases at glass transition because the chain segments are freely sliding from each other above glass transition temperature by virtue of single bond rotations. Therefore, above glass transition temperature, the polymer becomes more permeable for gas molecules and at the same time the selectivity of a polymer membrane decreases above the glass transition.

Our research focus is centered around the mechanism of glass transition in terms of its impact on polymer membrane's oxygen enrichment selectivity. We are working with polymers whose selectivity can be manipulated by introducing abundant polymer-nanofiller interfaces hoping to incite the secondary gas-separation mechanism which can ultimately affect the selectivity at above glass transition temperature. Polymer membrane above glass transition is a better material for gas molecules to dissolve and to diffuse but with lower selectivity.

Towards the end of understanding the oxygen enrichment by polymer membranes, we have first developed a molecular dynamics model which is capable of predicting the specific volumes thus the free volumes of a polymer at minimal potential energy. The potential energy of the chosen simulation system was calculated using the GROMACS implementation of the modified OPLS-AA force field in the following

equation. The force field parameters for PLA were obtained from O'Brien et al and the parameters for silica were taken from Wensink et al.

$$E_{PE} = \sum_{bonds} k_r \left(r - r_0 \right)^2 + \sum_{angles} k_\theta \left(\theta - \theta_0 \right)^2 + \sum_{impropers} k_\xi \left(\xi - \xi_0 \right)^2$$

$$+ \sum_{n=0}^{5} C_n \left(\cos(\Psi) \right)^n + \sum_i \sum_{j>i} f_{ij} \left\{ \frac{q_i q_j e^2}{r_{ij}} + 4\varepsilon_{ij} \left[\left(\frac{\sigma_{ij}}{r_{ij}} \right)^{12} - \left(\frac{\sigma_{ij}}{r_{ij}} \right)^6 \right] \right\}$$

The nontorsional bonded interactions are modeled by first three harmonic terms for bond stretching, angle bending, and out of plane deformations for planar groups. The force constants for intramolecular deformations $\left(k_r, k_\theta, k_\xi \right)$ define the magnitude of the energy required to move the internal coordinates $\left(r, \theta, \xi \right)$ away from their unstrained default values $\left(r_0, \theta_0, \xi_0 \right)$. The proper torsions are defined in terms of the specific dihedral angle (ψ) and Ryckaert-Bellemans potential parameter C_n, where n = 0, 1... 5. The non-bonded interactions are modeled by Coulombic and 6-12 Lennard-Jones terms, where r_{ij} is the distance of two sites, q is the partial atomic charge, and σ_{ij} and ε_{ij} are the Lennard-Jones parameters. The scaling factor f_{ij} is 1.0 for all non-bonded interactions except for the 1, 4-intramolecular interactions.

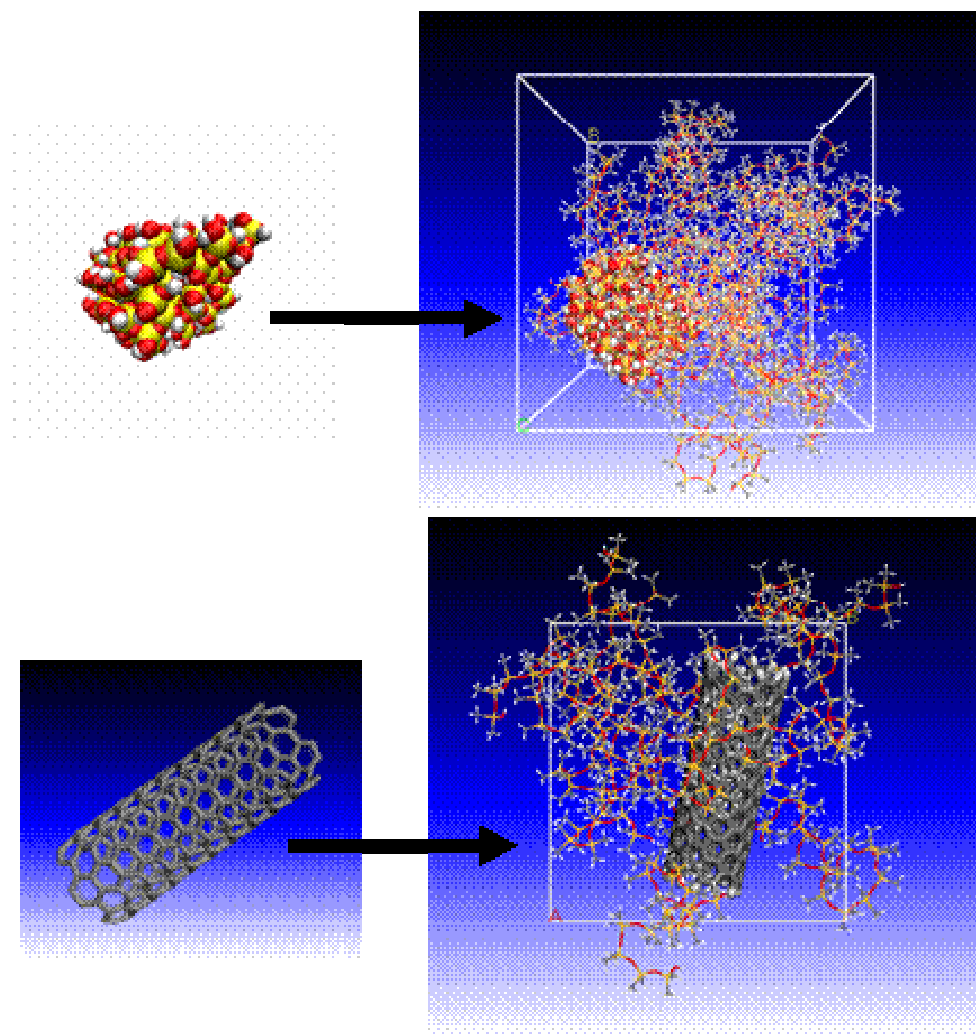A simulated model of these membranes is shown in Figure 7.

Figure 7. The molecular dynamics simulation models for nanosilica-filled polymer (top) and nanotube-filled polymer (bottom) for the purpose of predicting gas separation property.

4. RESULTS AND DISCUSSION

Membrane utilizing Matrimid 5218 polyimide backbone and a zeolite as the filler was fabricated on a porous stainless steel substrate. This membrane was exposed to pure N_2 and pure O_2 at 3.4 atm (50 psi) for two hours.

The resulting permeability was 0.114 Barrer and 0.380 Barrer, respectively, with a selectivity for O_2 of 3.33. After 12 hours, the results improved to a permeability of 0.093 for N_2 and 0.460 for O_2, with a selectivity for O_2 of 4.95. While the results are

still below required values, they show considerable potential that a mixed matrix polyimide membrane with zeolite nano-filler could meet the requirements necessary for commercial application in the future.

The pressure rising of permeating gas for polymer membrane in 2 hours was showed in Figure 8. The slopes of the two curves were calculated by linear regression. The slope of nitrogen was 1.54585E-6 psi/second and the slope of oxygen was 6.44114E-6 psi/second. The R values for regressions were larger than 0.99. Then the permeability was calculated. Permeability of nitrogen is 0.114 barrer. Permeability of oxygen is 0.380 barrer. The selectivity for oxygen is 3.33.
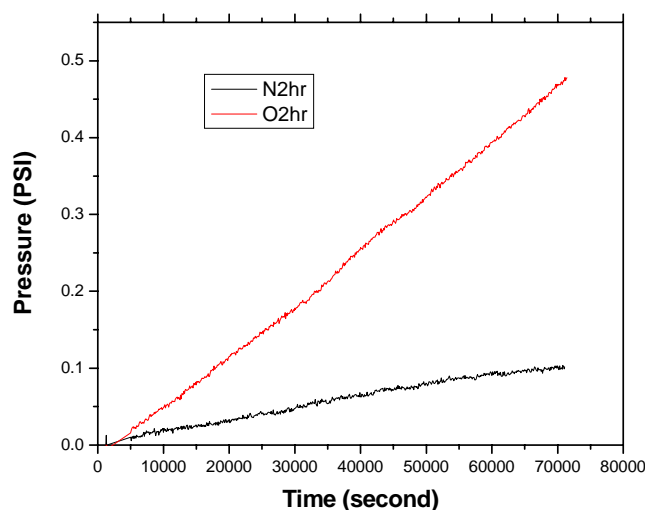

Figure 8. The pressure rising of permeating gas (Oxygen and Nitrogen, respectively) for polymer membrane in 2 hours.

The pressure rising of permeating gas for polymer membrane in 12 hours was showed in Figure 9. The slopes of the two curves were calculated by linear regression. The slope of nitrogen was 1.58134E-6 PSI/second and the slope of oxygen was 7.79679E-6 PSI/second. The R values for regressions were larger than 0.99. Then the permeability was calculated. Permeability of nitrogen is 0.093 barrer. Permeability of oxygen is 0.460 barrer. The selectivity for oxygen is 4.95.
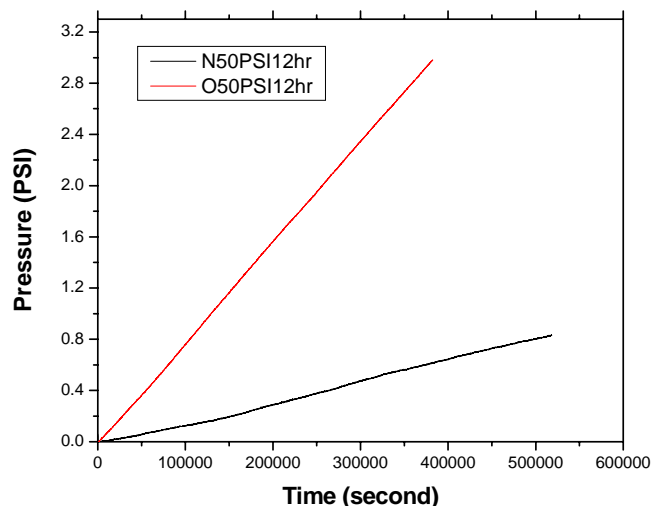
**Figure 9. The pressure rising of permeating gas for
polymer membrane in 12 hours.**

For the nano-fumed silica PDMS membranes, the fumed silica chosen was CAB-O-SIL TS-530. The hydrophobic silica was chosen because it had greater potential for proper mixing with the elastomer.   A series of neat PDMS membrane were prepared from SYLGARD$^{©}$ 184 (Dow Corning Corporation). The feed pressure is kept at 60psig and pure gas is used instead of mixed gases to reduce the number of variables in the experiment. The final results matches pretty well with the previous work as long as the neat PDMS is concerned. The fumed silica is amorphous synthetic silica produced by pyrogenic process from silicon tetrachloride in hydrogen and oxygen. Cabot makes both hydrophilic (untreated) and hydrophobic (treated) silica. We are using the treated one because it can mix better with the elastomer. The siloxane prepolymer was first diluted with toluene and then the silica fillers were added and thoroughly mixed using a glass rod. Following the addition of curing agent, the liquid solution was placed on a Fisher Scientific hot plate at 80 ^{o}C for 15 min to remove the toluene. Then the solution was placed in a Branson 5510 ultrasonic cleaner to remove any air bubbles for 20 min until most of the air bubbles were removed. （The solution will become more viscous） After that, the solution was cast on a paper sheet placed on a glass plate to cure. The curing process was done in a ventilated hood for more than 24 hours at room temperature. The fumed silica did not produce good dispersion in the polymer, resulting in limited success. The O_2 selectivity observed for 1% and 2.5% fumed-silica at 4.1 atm (60 psi) was 2.72 and 2.81, as well as 10.5 respectively but with unsatisfactory reproducibility.   Although it is an improvement over the O_2 selectivity of 2.54 for neat PDMS, the use of the nano silica for this membrane was rather difficult because the graduate student could not

reproduce some of the high selectivity experiment and the membrane tends to vary batch to batch.

For the nanotube-polymer membrane, we achieved selectivity of 0.86 for PDMS filled with single-walled carbon nano-tubes. When compared to pure PDMS, with a selectivity of 1.97, it is apparent that this filler is not appropriate for the purpose of this project.

The membranes being researched have several desirable properties, including high glass transition temperatures, high thermal and structural stability, high selectivity (0.460 Barrers), and high permeability (4.95). In addition, capital costs are low, due to the absence of precious metals found in many other membrane technologies.

The model predicted the dependence of the self diffusion constant as a function of the degree of polymerization, as shown in Figure 10 [3, 4].
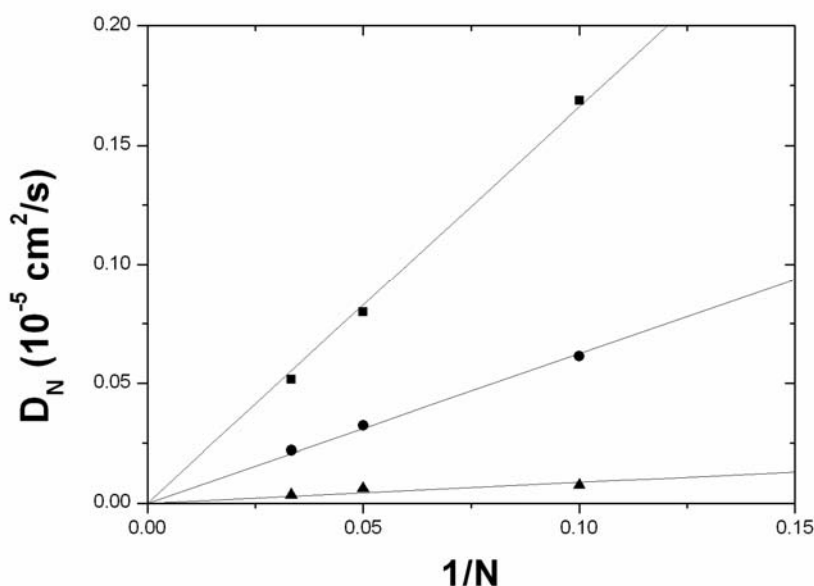

**Figure 10. Plot of self diffusion constant D_N versus reciprocal
different degree of polymerization 1/N (From top to bottom
T=500K, T=450K and T=400K)**

5. CONCLUSION

We have accomplished the following:

- Performed permeation and diffusion experiments using polymers with nano-silica particles, nano-tubes, and zeolites as fillers.

- Studied the influence of nano-fillers on the self diffusion, free volume, glass transition, oxygen diffusion and solubility, and perm-selectivity of oxygen in polymer membranes.
- Developed molecular models of single-walled carbon nano-tube and nano-fumed silica PDMS membranes, and zeolites-modulated polyimide membranes.
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6. GRAPHICAL MATERIALS LIST

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