Mixed Matrix Membranes for Efficient Gas Separation

Research Experience for Teachers

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Abstract

Polymers are long chain-like molecules that can be thousands or even millions of times larger than other molecules. Polymers, like proteins, starches, and DNA, are essential to all life, but plastics are polymers, too. Although they are often thought of as environmentally unfriendly, plastics can help slow global warming.

In the U.S., 4,500 trillion Btu of energy, or about 22% of all power plant output, is used to separate industrial gases. Using polymer (plastic) membranes to separate those gases would require much less energy.[2] Additional benefits of polymer membranes include low cost, a compact design with no moving parts, and low environmental impact. Triptycene-containing polyimides are an interesting new group of polymers. The unique 3-D shape of the triptycene molecule, consisting of three "blades" protruding from a single hinge, creates high amounts of space throughout the polymer, which leads to good gas separation properties.

Figure 1: The membrane gas separation unit, circled in yellow, is much smaller than the two towers, which use traditional gas separation, but it can complete the same separation comparably. (*Photo courtesy of Air Liquide)

Figure 2: Triptycene

Mixed matrix membranes (MMMs) are polymer membranes that have inorganic fillers dispersed throughout. MMMs are easier to process and manufacture than inorganic membranes and are expected to have increased gas separation properties compared to polymer membranes. Zeolites are crystalline molecules made up of silicon, aluminum, and oxygen and are very good at absorbing small molecules. They are used in pet litter, wastewater treatment, detergent, for water purification, and are one type of inorganic filler added to MMMs. Another type of filler is metal organic frameworks (MOFs). MOFs are hybrids of organic and inorganic materials that have properties similar to zeolites, but they can be "tuned" to certain pore sizes, and they have better affinity for polymers.

In this investigation, MMMs were produced by mixing the triptycene-containing polyimide, 1,4-triptycene_para-6FDA, with varying amounts of zeolite 4A and zeolite ZSM-5. The films were imaged using scanning electron microscopy (SEM) to observe the distribution of the particles in the membrane and the interaction between the zeolite and the polymer. Preliminary findings suggest some void space between the particles and the polymer that could decrease gas separation performance, which will be investigated further with gas permeation measurements. Additionally, the films were tested using thermal gravimetric analysis (TGA) and found to be very thermally stable, breaking down around 500°C. Along with the zeolite work, a metal organic framework (MOF), called ZIF-90 was also synthesized to be incorporated into future MMMs. Testing of the ZIF-90 particles are in progress.

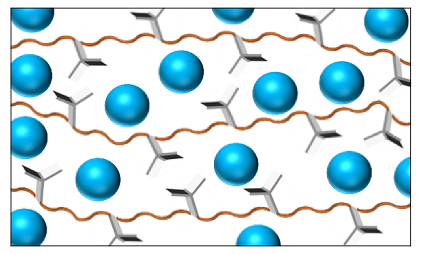


Figure 3: Anticipated arrangement of zeolite dispersion in triptycene-containing polymer

Discussion

Theoretically, the gas separation properties of MMMs should be superior to polymer membranes, due to the inorganic fillers' high gas separation capabilities. However, voids around the particles could allow gases to bypass the pores in the zeolites, thus decreasing gas separation properties. The only way to determine the effect of the zeolites and the voids is through gas permeation measurements.

Future Work:

- MMMs with varying amounts of zeolite 13X and ZIF-90 need to be made using the 1,4 triptycene-para-6FDA polymer.
- MMMs with varying amounts of zeolite 4A, 13X, ZSM-5, and ZIF-90 need to be made using other triptycene-containing polyimide polymers.
- The gas selectivity and permeability properties of all of the hybrid films created need to be tested using a constant-volume variable pressure method to determine the impact of adding inorganic fillers to the polymer membrane.
- Characterization of the ZIF-90 particles needs to be completed

Connection to the Classroom

The work performed this summer has multiple connections to the biology or environmental science classroom, and it was difficult to decide on only one curriculum project. On the one hand, membranes were created and one unit of study in biology reflects the importance of membranes in regulating cell activities.
But on another, those membranes are made up of polymers and the dry weight of living organisms is primarily protein, which is a polymer, and the instructions for life are written on another polymer, DNA. Also, these polymer membranes are being created to separate gases from one another, saving energy and reducing the amount of harmful greenhouse gases being put into the atmosphere, which plays to a focus on environmental science for the curriculum project. In the end, a curriculum project was created for biology, in which students are introduced to polymers during the biochemistry unit, and another was made for environmental science. Both are highlighted below.

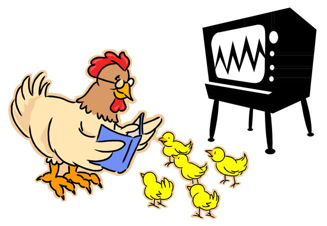
Biology Curriculum Highlights

Indiana State Biology Standards: B.1.1, B.5.1, B.5.4

Activity 1: Students are introduced to polymers by constructing models of monomers using gumdrops and toothpicks.

Lab 2: Slime is an easy polymer for students to make in the classroom, using school glue, borax, and water.

Demonstration 3: A natural plastic will be made using milk and vinegar. It will demonstrate the similarities between natural and synthetic polymers.



In addition, students will watch two short videos about polymers and read about how the history of rubber relates to the discovery of macromolecules.

Production of 1,4 triptycene_para-6FDA/zeolite mixed matrix membranes

- Calculated weight needed to achieve 5%, 10%, 15%, and 20% total weight of the zeolites and 1,4-triptycene-para-6FDA.

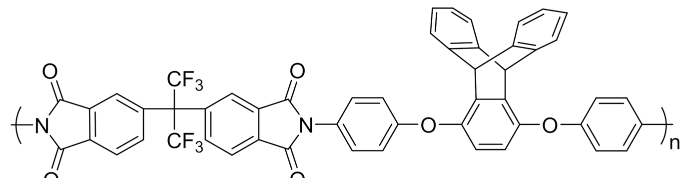


Figure 4: 1,4-triptycene-para-6FDA

Figure 5: Zeolite solution in the sonicator

- Added solvent to the zeolite and polymer separately and stirred.
- Filtered the polymer and sonicated the zeolite.
- Stirred the polymer and slowly added the zeolite.
- Allowed the mixture to stir for almost 24 hours.
- Sonicated the mixture for 30 minutes.
- Cast films and allowed to air-dry overnight.
- Dried the films in a vacuum oven for 24 hours.
- Soaked the films in methanol to remove any remaining solvent.

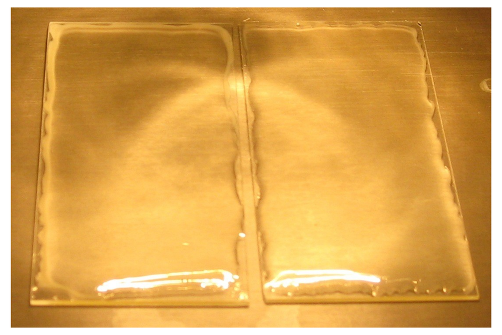


Figure 6: Recently cast 5% zeolite ZSM-5/6FDA-1,4-trip_para films

Synthesis of ZIF-90

- Measured, stirred, and filtered imidazolate-2-carboxyaldehyde (ICA).
- Measured and stirred zinc acetate dehydrate.
- Added the zinc acetate dehydrate to the ICA, then stirred.
- Centrifuged the mixture.
- Washed the ZIF-90 with methanol to remove the solvent.
- Allowed the methanol to evaporate and dried product in the vacuum oven.

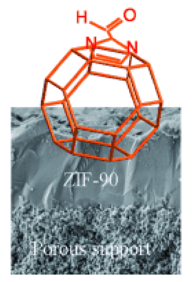


Figure 7: ZIF-90 above an SEM of a ZIF-90

Results

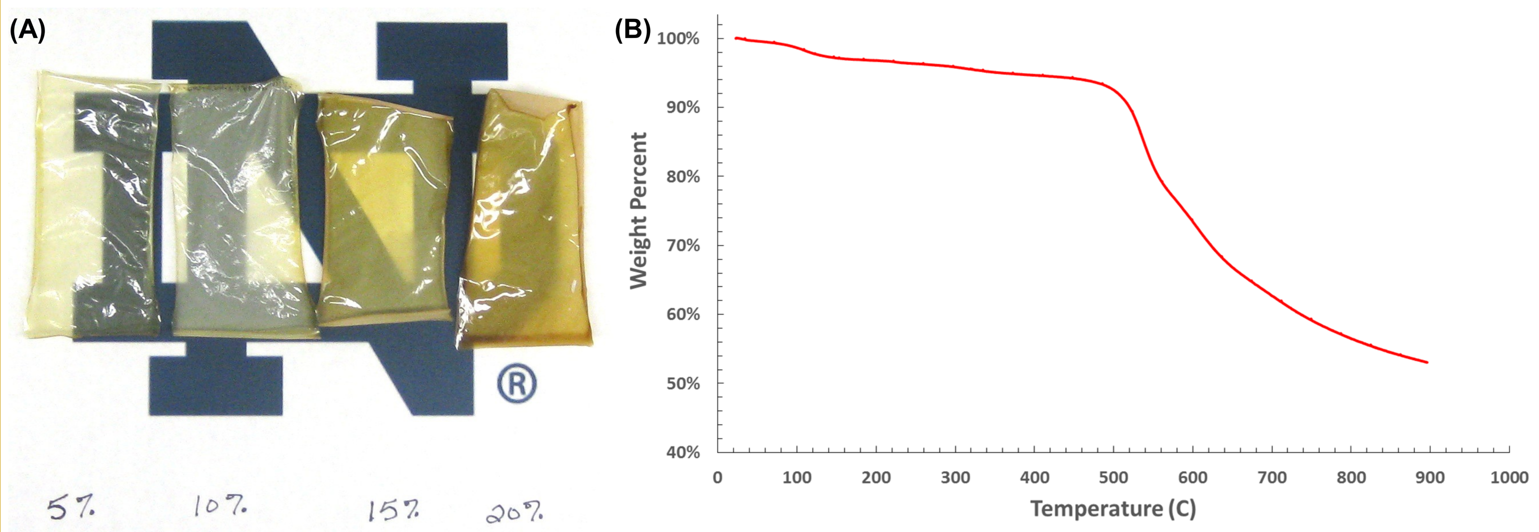


Figure 8: (A) As the zeolite content was increased in the MMMs, the membranes became more opaque. Left to right: 6FDA-1,4-trip_para MMM loaded with 5% zeolite 4A, 10% zeolite 4A, 15% zeolite 4A, 20% zeolite (B) Graph produced by TGA of 5% zeolite 4A loading in 6FDA-1,4-trip_para.

The membranes were tested using thermal gravimetric analysis (TGA), which showed them to be very thermally stable, breaking down around 500°C. The membranes were imaged using a scanning electron microscope (SEM). The images suggested that some of the zeolite particles may have clustered together and it appeared that a significant portion of the zeolite particles had settled to the bottom of the membrane. Therefore, the zeolite particles may not be evenly distributed throughout the membrane. Small voids surrounded many of the zeolite particles.

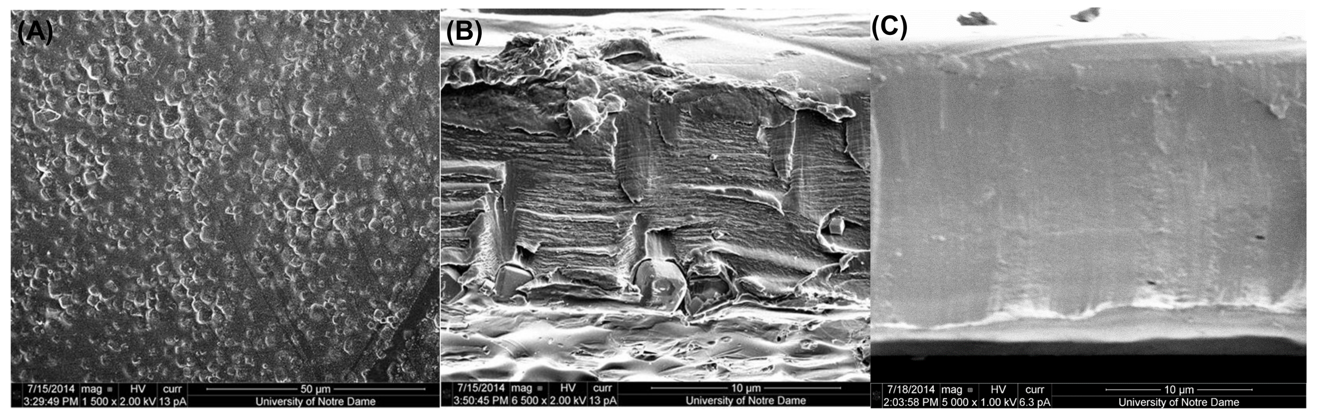
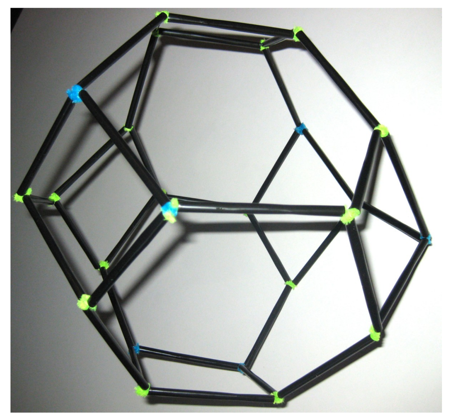


Figure 9: (A) Bottom surface of the 5% zeolite 4A/1,4-triptycene_para-6FDA. (B) Cross-section of the same membrane. (C) Cross-section of a 1,4-triptycene-para_6FDA membrane with no zeolite particles for comparison.

Environmental Science Curriculum Highlights

NGSS: HS-PS2-6, HS-LS2-7, HS-ESS3-2, HS-ESS3-4.



Day 1: The students will be shown a model of a zeolite molecule, then they will observe the water softening effects of zeolites on distilled water, tap water, and $CaCl_2$ solution during a teacher demonstration. Next, the students will use natural zeolites to remove ammonia from water. Finally, the student will perform an inquiry on zeolites' capacity to remove other substances from water.

Day 2-3: Students will write a paragraph or draw a picture to describe how they think wastewater is cleaned. Then, they will develop strategies, including the potential use of zeolites, to remove contaminants from simulated "wastewater." Finally, the students will compare their strategies to one another's and to contemporary wastewater treatment plants.

Day 4: Cleaning air will be compared to cleaning water and the separation potential of membranes in reducing air pollution and global warming will be discussed. To demonstrate that, four beakers will be filled with equal amounts of water and covered with different types of plastic polymer membranes (different brands of plastic wrap). The rates of water evaporation through the membranes will be observed and recorded.

References

1. Huang, N. Wang, C. Kong, and J. Caro, *Angew. Chem. Int. Ed. Engl.*, 2012, **51**, 10551–5

2. Sanders, D. Smith, Z. Guo, R. Robeson, L. McGrath, J. Paul, D. Freeman, B. *Polymer*, 2013, **54**, 4729-4761

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