

IOWA SPACE GRANT CONSORTIUM
“Seed” Grant - PY15

Project Title: Flexible Systems for Membrane Separations Using Photocontrolled Smart Materials.

Total ISGC \$'s Requested: \$10,000

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Summary: Preliminary studies to investigate photocontrolled smart systems were carried out. As a direct result of this seed grant, we have developed a direct collaboration with Dr. Michael A. Meador, chief of the Polymers Branch at the John Glenn Research Center. This has also indirectly led to the graduate student working on this project (John Elliff) applying for and receiving a 3 year graduate fellowship (GSRP) from NASA. During the past year John spent one month as an intern at NASA Glenn working directly with out colaaborators there. Also, the two undergraduate students (Jaqueline Alcantar and James Aberg) have been involved in the lab setup and initial syntheses steps in the development of the photoresponsive materials.

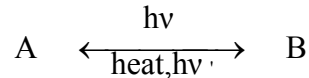
Two polymer systems are being developed in the program. The first involves the use of photoresponsive polymers for use as controllable membranes. The second polymer system is a shape changing material for use in aerospace applications. This research is being carried out in conjunction with Dr. Michael A. Meador, chief of the Polymers Branch at the John Glenn Research Center.

Project Description

In recently announced NASA missions such as the proposed lunar landings and manned Mars missions, there will be a need for smart materials that can sense their environment and respond to meet those conditions. Applications requiring these materials include propulsion and communication systems, where the material will be required to change shape or physical characteristics. These smart materials can also be incorporated

into membranes for use where tunable properties such as porosity and diffusivity are required. Photoresponsive polymers are being investigated as smart, adaptive materials.

A photo responsive polymer (A) can be transformed into an isomer (B) by radiation with UV light.



This is an equilibrium conversion where the isomer can be returned to its original state either thermally or by irradiation with visible light (1-4). It has been demonstrated that these photoresponsive materials can be incorporated into photomechanically responsive materials. Also, they can be incorporated into swellable hydrogels for membrane use (2-4). In the ongoing work, the response of photomechanically adaptive materials will be increased and optimized by layering the photoresponse with other materials taking advantage of the differential length change to create mechanical leveraging. Determining the optimal photochrome concentration can maximize this leveraging response. Simple models will be used that correlate dimensional changes with observed response. Likewise, the porosity and diffusivity in hydrogels and will be determined and optimized. The objectives of the ongoing research are;

1. To develop photoresponsive separation membranes which can be controlled in real time and determine the mechanism by which the photoresponse modifies the permeability of the membrane.
2. To develop photoresponsive composite materials that can respond to real time photo-stimulus to change their spatial dimensions.
3. To develop models that predict and correlate observed properties to a particular photochrome concentration.
4. To develop modules incorporating these materials that are compact, reliable and potentially suitable for utilization in an environment such as the lunar surface and interplanetary space.

Significance and Impact at NASA

1. Photomechanical Systems

Solid photomechanical systems may be useful in changing the surface characteristics of air intakes and airframe components, thereby changing the fluid flow

characteristics through and around these components. For these systems a bulk composite material where the outer layer is a photoresponsive polymer may be useful. The UV light can be delivered through a network of fiber-optic cables. In addition, the inclusion of these photochromes into the polymer backbone of block copolymer systems will enhance their response.

The development of these materials would offer significant advantages over conventional “smart” materials. Past efforts in developing adaptive materials have focused on materials responsive to thermal stimuli. The development of photo responsive polymers will allow for decreased response time (the velocity of light vs. heat flow) and lighter materials due to the low relative density of polymers. This will serve to enhance the overall performance of the systems utilizing these materials.

2. Membranes

Membranes are important for a broad range of applications ranging from water purification, to gas separations (air purification) and protein recovery. Examples of current uses that may be of direct interest to NASA include reverse osmosis, carbon dioxide removal with oxygen recovery, hemodialysis, blood oxygenation, and the preparation of pyrogen free water. To carry out this broad range of separations would generally require a large number of different membranes. In an environment such as a moon base or interplanetary craft, this luxury is not available. Clearly, in a situation where space is limited and weight is a premium, it is not possible to carry every possible membrane that may be needed.

The development of a membrane with controllable permeability would provide significant advantages over standard membranes for aerospace applications. The primary advantage would be the ability to alter the membrane properties while in operation. Thus, only a few types of membranes could be used to carry out a broad range of separations. Photoresponsive membranes may provide the capability to allow this flexibility.

Experimental Design

Both of these projects must be optimized for photoresponse as a function of;

1. Choice of polymeric material and photochromic crosslinking agent.
2. Photochrome concentration.

3. Penetration depth of photons into the material as a function of UV radiation intensity and wavelength.

These functions are not mutually exclusive but each of these responses will be discussed separately along with their significance to each project.

1. Choice of Polymeric Material

In the optimization of photo responsive membranes, previous work by Kodzwa and Rethwisch will be extended to complete the characterization of a membrane composed of polyethylacrylate PEA with the photocromic spiropyran 1,1' (α , α' -p-xylyl)-bis-[3,3 dimethyl-8-methacryloxymethyl-6-nitro-spiro(2H-1-benzopyran 2,2'-indoline)], "xylene bis-DIPS" as a crosslinking agent. This membrane has been observed to contract 2-5% when irradiated with UV light (290-380 nm) (5).

2. Photochrome Concentration

Prior membrane work using PEA-xylene bis-DIPS compounds have focus on crosslinking agent concentrations from 0-1 mole %. It has been shown there is a more pronounced photocontractive response as photochrome concentration was increased. This study will determine the response in the domain of 0-5 mole % of photochrome. It is expected that this domain should encompass the range where UV absorbance will become the dominant limit on response. Properties that will be measured include permeability, diffusivity, solubility and Young's modulus.

3. Photon Penetration Depth

The PEA-xylene bis-DIPS membranes are photocontractive at UV wavelengths of 290-380 nm. The response will be studied as a function of mono-disperse wavelength. As shown by Beer's law, when the extinction coefficient is reduced "off peak", there will be an increase in the depth the photons will travel into the photo responsive material before complete absorbance. The optimal path length will occur in this 290-380 nm range. The reverse reaction, (expansion to original state), takes place in visible light ($\lambda > 472$ nm). Similarly this reaction will be optimized at a monodisperse wavelength, and determinations of response will be made for photomechanical materials.

Development of the synthesis procedure for the bis-DIPS compound has been ongoing. The primary focus on this synthesis was carried out at the University of Iowa. John Elliff then conducted research at the Glenn Research Center from Oct. 17, 2004

until Nov. 12, 2004. This work was done in collaboration with Dr. Michael Meador and Dr. Daniel Tyson and focused on the synthesis of the bis-DIPS. During this visit, preliminary steps in the synthesis of the compound were completed and the products were characterized by NMR. Synthesis of the bis-DIPS compound is ongoing in consultation with several faculty members in the Department of Chemistry at the University of Iowa. Current efforts include determination of the correct reaction conditions that will yield the desired product.

Other research carried out at GRC was to expand prior work at NASA Glenn on photoresponsive materials that undergo rod-coil transitions. This work involved the casting of gels that incorporated azo-benzene molecules into Jeffamine coils of varying molecular weight. Further testing of these gels at the University of Iowa verified the results obtained by the Glenn Research center. We are now developing systems that will provide a greater photoresponse.

Polyethylacrylate gels have been cast using methylene bis-acrylamide as a crosslinking agent. The resulting gels were defect free when the polymerization conditions were oxygen free and at a temperature that allowed the evolving nitrogen gas to diffuse through the reaction mixture without creating bubbles in the mixture. This method will be directly transferred to the casting of the photo responsive gels.

In order to measure the photoresponse, and permeability of hydrogels, a diffusion cell has been constructed (Figure 1). This diffusion cell incorporates quartz windows, a 500 W Oriel mercury lamp and a cutoff filter which eliminates wavelengths below 270 nm. The cell is immersed in a water bath to insure isothermal conditions. Solutions from both sides of the cell will be continuously circulated to a Hewlett-Packard 8452A UV/Vis spectrophotometer. Ionic concentration in both cells will be determined using ion selective electrodes. The membrane permeability for a given species will be experimentally determined by plotting concentration vs. time as:

$$\ln \left[\frac{c_t^1 - c_t^2}{c_o^1 - c_o^2} \right] = -\frac{2PA}{V} t$$

where P is the permeability, A is the membrane area, c is the cell concentration and V is the volume of the cell.

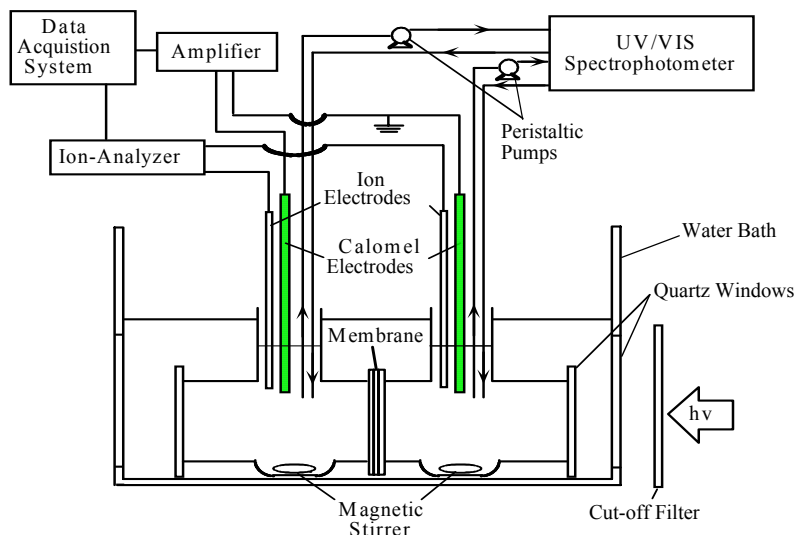


Figure 1. Diffusion Cell

Future Research Plans

Synthesis of the spiropyran crosslinking agent will proceed. When completed, this spiropyran will be incorporated into a polyethylacrylate hydrogel in concentrations ranging from 0-5%. These membranes will be characterized as to mechanical strength, diffusivity, porosity and charge density.

Efforts in the development of photo-mechanically responsive materials are ongoing. With the determination of the lack of photoresponse of the azo-benzene-Jeffamine gels, there are several other methods to be investigated. These include the incorporation of azo-benzene units into Kevlar chains where the response should be similar to, but more pronounced than the Jeffamine compounds, and the development of a photo-expansive dye. This expansion will be possible if the photoresponse involves a ring opening isomerization similar to that of spiropyran compounds (5). If this dye is developed it can be layered onto a photo-contractive material thereby utilizing these competing responses to achieve photomechanical leveraging.

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