Separation of CO_2 and N_2 with a Composite Perfluorocyclobutyl Polymer Membrane

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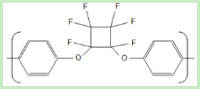
Introduction

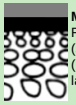
- Humans emit one trillion tons of carbon into the air every year
- One method of capturing CO_2 from post-combustion processes is to use thin-film composite membranes
- Glassy polymeric membranes are particularly well-suited to gas separation due to a good balance of permeability and selectivity
- However, they are also affected by issues such as aging and plasticization effects, especially in thin films

Objectives

- Explore effects of selective layer thickness of perfluorocyclobutyl (PFCB) polymer composite membranes on CO_2 plasticization
- Test membrane permeance for single gas (CO_2 and N_2) and CO_2/N_2 mixed-gas mixtures

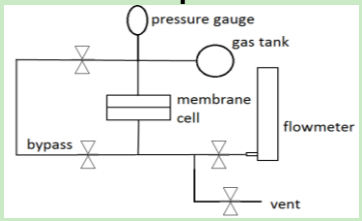


PFCB biphenylvinyl ether (BPVE).



Membrane cross-section: From top to bottom: PFCB (selective layer), gutter layer (proprietary material), support layer (PAN50)

Experimental Methods



Schematic of gas testing apparatus.

Large and small cells for gutter layer and PFCB testing, respectively.

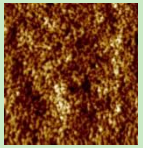
- Dip-coat membranes in 0.30wt% gutter layer solution
- Dip-coat in PFCB/chloroform solutions of 0.25-1.00wt% and withdrawal speeds of 100 mm/min or 211 mm/min
- Measure permeance of composite membranes at 20-500 psi
- Calculate permeance of PFCB layer using

$$Perm = \frac{flux}{\Delta p} = \frac{P}{\sigma} = \frac{1}{r} = \left(\frac{\sigma_a}{P_a} + \frac{\sigma_b}{P_b}\right)^{-1}$$

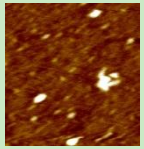
where Perm = permeance, p = pressure, P = permeability, σ = thickness, and r = resistance

Results

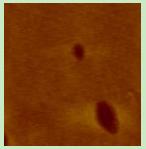
- **Support layer**: highly permeable; slightly selective for N_2 over CO_2 due to its lower molecular weight
- **Gutter layer**: ideal CO_2/N_2 selectivity = 5; CO_2 permeance of 1300-1800 GPU



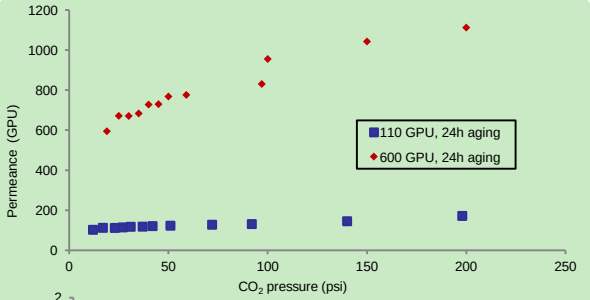
PAN50 membrane
1 x 1 um. Porosity = 50%. RMS = 2.5 nm.



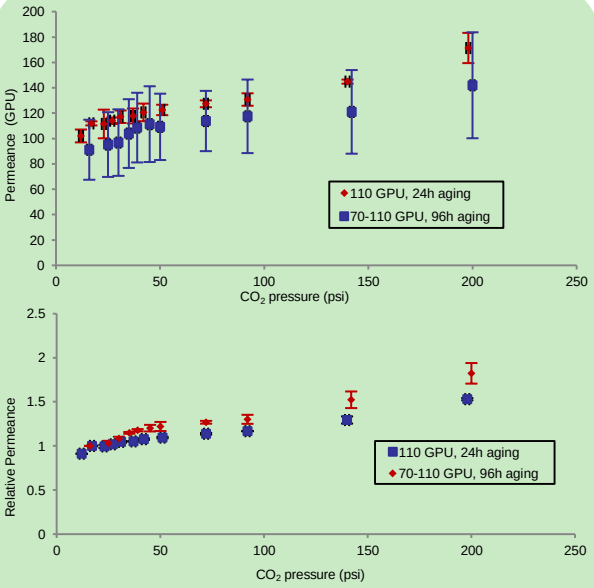
Plasma-treated gutter layer membrane
1 x 1 um. RMS = 1.5 nm.



PFCB coated membrane
1 x 1 um. 50 to 80 nm thick. RMS = 1.1 nm.



- Thinner membranes (higher permeance) show greater increase in permeance – greater plasticization
- Difference is especially dramatic at higher pressures



- There does not seem to be a significant difference between the two curves, despite different aging
- This is against expectations

Conclusions

- In accordance with expectations, thinner membranes plasticize more quickly
- Our preliminary tests seem to indicate that aging does not affect permeance

Future Work

- Further studies should continue to explore the effect of thickness and aging on plasticization
- PFCB swelling in CO_2 should be studied using ellipsometry

Acknowledgements: *This work was part of the Advanced Functional Membranes Research Experiences for Undergraduates program at Clemson University. Support for this REU program was provided by the National Science Foundation under award EEC 1061524.*

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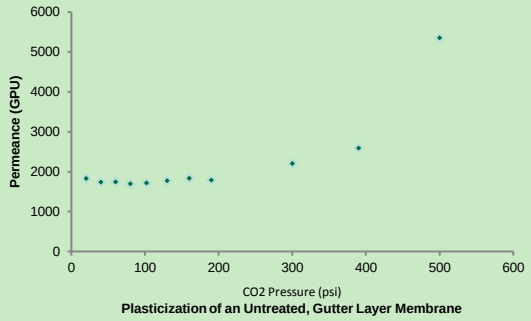

Plasticization of an Untreated, Gutter Layer Membrane

- No significant plasticization until 300 psi
- Gutter layer permeance increases to 2-3 times its value at 20 psi