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Poly(ether-*block*-amide) Copolymer Membrane: Gas Separation and Pervaporation

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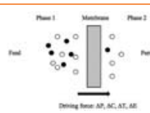
Research Objectives

- Investigate intrinsic gas permeability properties of Pebax®1074 copolymer
- Determine effects of pressure, temperature, and other variables on gas permeation
- Study water and dimethyl methylphosphonate (DMMP) liquid permeability properties to establish feasibility of Pebax®1074 as chemically resistant protective material

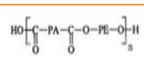
Background Information

Membranes



- Permselective barrier between 2 phases
- Separation is achieved when one species permeates faster across the membrane than the other components

Pebax®1074



- Breathable thermoplastic elastomer
- 45 wt.% rigid polyamide 12 (PA12), 55 wt.% soft polyethylene oxide (PEO)
- T_g = -55 °C, rubbery at room temperature
- Contact angle 70°, slightly hydrophilic

Solution-Diffusion Mechanism

Mass transport for nonporous membranes, comprised of 3 steps:

1. Penetrant adsorption and dissolution at the polymer membrane feed interface,
2. Diffusion of penetrant through the polymer matrix, and
3. Desorption of penetrant into the other side of the membrane

Fick's first law - Flux

$$J_A = -D_A \frac{dC_A}{dx}$$

Permeability coefficient

$$P_A = \frac{J_A}{\Delta p / l}$$

Ideal selectivity

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

Temperature

Arrhenius relationship

$$P = D_0 \exp\left(\frac{-E_D}{RT}\right) S_0 \exp\left(\frac{-\Delta H_s}{RT}\right)$$

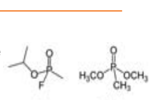
$$P = P_0 \exp\left(\frac{-E_p}{RT}\right)$$

Activation energy of permeation

$$E_p = E_D + \Delta H_S$$

Pervaporation

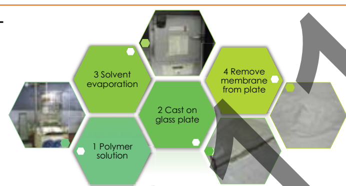
- Pervaporation = permeation + evaporation
- Transport driven by vapour pressure difference across the membrane
- Challenge chemical is dimethyl methylphosphonate (DMMP)
  – nontoxic organophosphorus simulant of chemical nerve agent sarin



Experimental Methods

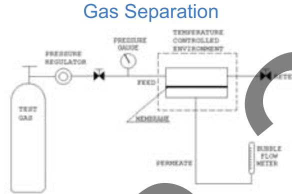
Membrane Preparation

- Polymer solvent: N-methyl-2-pyrolidinone (NMP) or butanol
- 15 wt.% solution
- Solution-casting technique
- Result in nonporous, symmetric, free-standing membrane



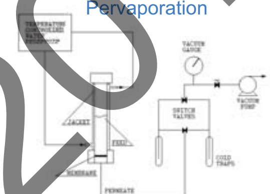
Membrane Testing

Gas Separation



Gases tested: N_2, O_2, CH_4, He, H_2, CO_2

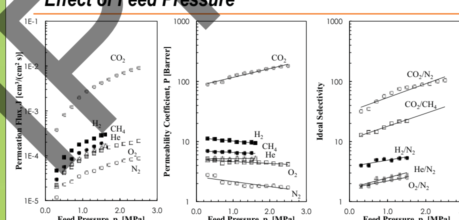
Pervaporation



Materials tested: Pebax®1074, Pebax®2533, nitrile, PVC, latex, LDPE, silicone, silicone-polycarbonate copolymer

Gas Separation

Effect of Feed Pressure

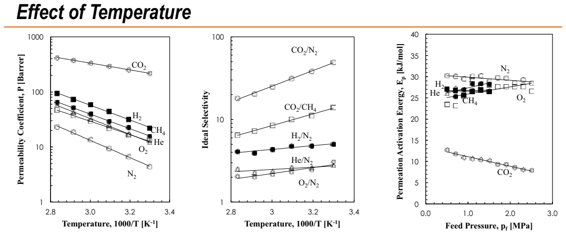


Gas	Size		Condensability	
	V_c (cm³/mol)	d_k (Å)	T_b (°C)	T_c (°C)
N_2	89.8	3.64	77.4	126.2
O_2	73.37	3.46	90.17	154.58
CH_4	98.6	3.82	111.66	190.56
He	57.30	2.6	4.30	5.19
H_2	64.2	2.89	20.27	32.98
CO_2	94.07	3.30	194.7	304.12

- ↑ size ↓ diffusivity
- ↑ condensability
  ↑ solubility

- Hydrostatic pressure reduce polymer free volume and penetrant diffusion
- Plasticization increase polymer free volume and elevate diffusion

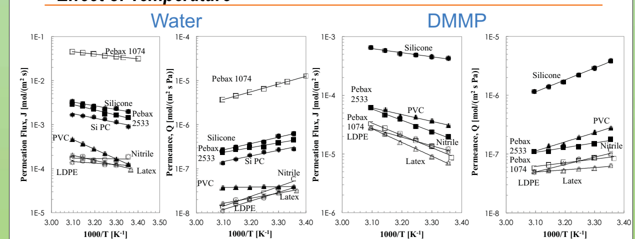
Effect of Temperature



- Increased temperature causes polymer chains to gain increased segmental motion resulting in more diffusive jumps conducted by the penetrants

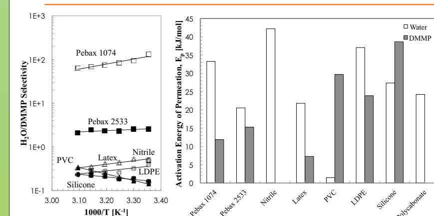
Pervaporation

Effect of Temperature



- Increased temperature results in higher vapour pressure difference across the membrane, plasticization, and more energized penetrant molecule

Membrane Materials



Property	H_2O	DMMP
Molecular weight (g/mol)	124.08	18.01
Boiling point (°C)	181	100
Saturated vapour pressure (Pa) @ 25 °C [c]	110.93	3187.7
Liquid density (g/cm³) @ 25 °C	1.145	1.00
ΔH_{vap} (kJ/mol) @ 25 °C	52.8	1.882

- Favourable interaction between H_2O and PEO block in Pebax®1074
- H_2O smaller and more volatile than DMMP

Conclusions

- High polar/nonpolar gas selectivities due to high solubility selectivity
- Increase in feed gas pressure causes compaction reducing permeability of non-condensable penetrant
- Increase in temperature results in an increase in permeability and decrease in selectivity
- Pebax®1074 is the most breathable and resistant to DMMP attack of all materials tested

Acknowledgement

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