Exploring the Role of Block Copolymer Properties in Enhancing CO_2 Absorbance of Supported Ionic Liquid Membranes

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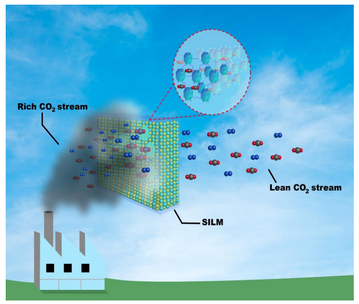
Introduction

- Block copolymers can mitigate the drawbacks of current supported ionic liquid membranes (SILMs) made from homopolymers for industrial CO_2 capture.
- SILMs are composed of an ionic liquid (IL) suspended in a polymer membrane which harnesses the physical and chemical properties of the IL to capture CO_2.
- Homopolymer SILMs have limited thermal stability, mechanical strength and flexibility, and inherent tradeoffs between permeability and selectivity.
- Block copolymers can overcome these weaknesses by balancing the properties of individual monomers to create a more mechanically robust and efficient SILM.
- PEBAX® copolymers have excellent elasticity, thermal stability, chemical resistance, and gas permeability. Block copolymer SILMs have the potential for industrial applications in CO_2 capture.

Experimental Methods

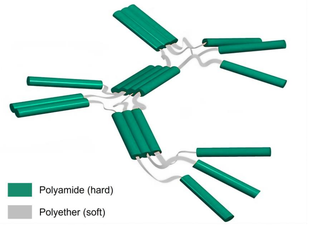
- PEBAX® 1657, PEBAX® 2533, and PEBAX® RNEW are synthesized at 3% weight for QCM absorbance testing and image analysis
- Solution is heated and stirred for 24 hrs before [EMIM][N(Tf)2] is added and stirred for an additional 24 hrs.
- Solution is poured into mold and dried under vacuum conditions for 48 hrs at 80 °C



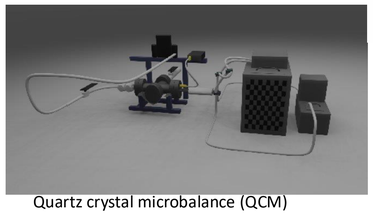
Materials

- PEBAX® Block Copolymer
- Polyamide - rigidity, mechanical strength, and thermal resistance
- Polyether - elasticity, flexibility, and low temperature properties

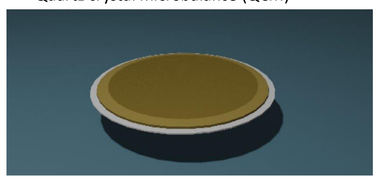
- Ionic liquid [EMIM][N(Tf)2]
- Cation: 1-Ethyl-3-methylimidazolium [EMIM] :Low viscosity and vapor pressure, high CO2 solubility
- Anion:bis(trifluoromethylsulfonyl)-Imide-[Tf2N]: Moisture stable and water miscible, high CO2 solubility



PEBAX® Polymers



Quartz crystal microbalance (QCM)



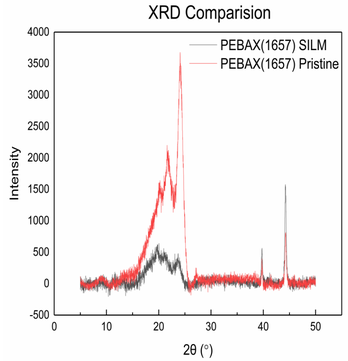
PEBAX® coating on quartz crystal

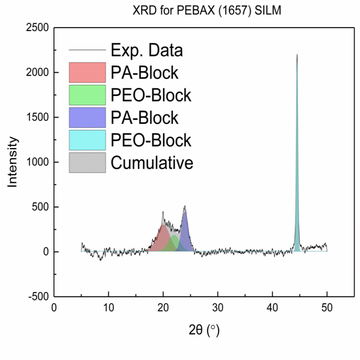
Quartz Crystal Microbalance

- Precise, real-time mass measurements at the picogram and nanogram level by measuring the change in resonant frequency of the quartz crystal.
- Changes in mass at different pressure and temperatures show the ranges and ideal conditions for CO_2 capture.

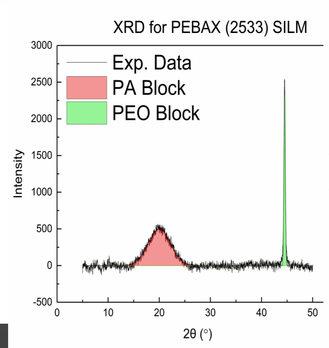
Crystallinity Index

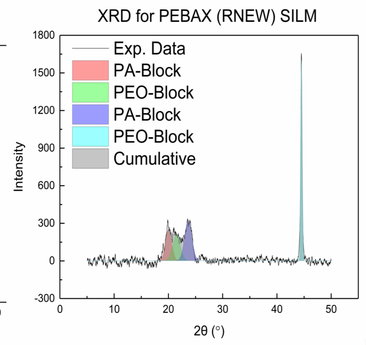
- Crystallinity measures how highly ordered and repeating the polymer chain is structured
- Higher crystallinity is correlated with improved selectivity and mechanical strength
- Lower crystallinity is correlated with increased permeability
- XRD analysis was used to determine crystallinity

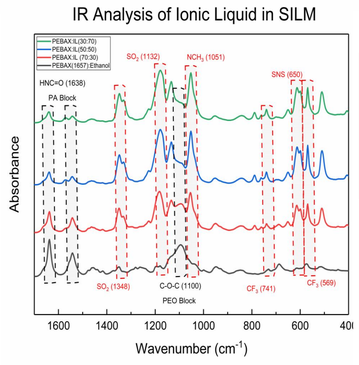




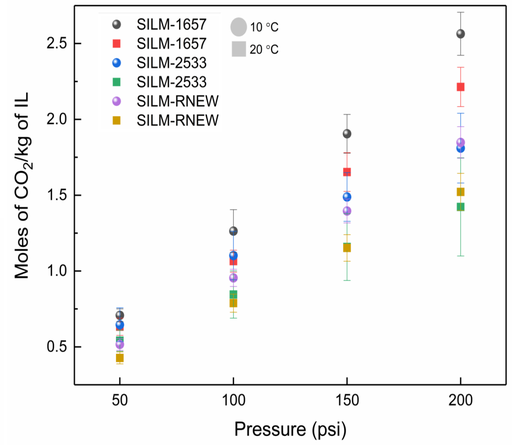
XRD for PEBAX (RNEW) SILM







PEBAX® (Grade)	Crystallinity Index
1657	36%
2533	39%
RNEW	38%

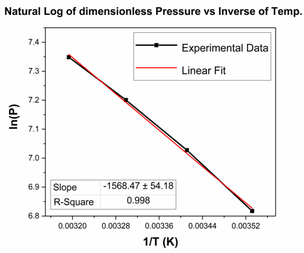


Heat of Sorption

- The heat of sorption is a measurement of how much the thermal energy of the membrane changes as CO_2 is adsorbed or absorbed
- Heat of sorption measurements can be used to determine how strongly the gas molecules and membrane interact

$$\frac{dln(P/P_o)}{d(1/T)} = \frac{-\Delta H_{ads}}{R}$$

Clausius-Clapeyron Equation



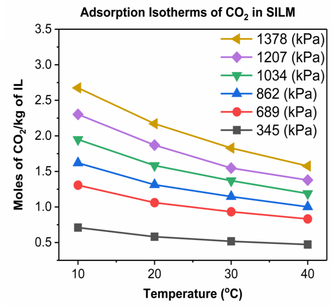
PEBAX® Grade vs CO_2 Absorbance

- The PEBAX® grade used to support the IL impacts SILM's CO_2 sorption
- Samples were tested at 10, 20, 30, and 40°C from 0-200 PSI.

- The PEBAX® 1657 SILM was able to capture the most CO_2 and was most effective at 10 °C.

Heat of Absorption ($-\Delta H_{ads}$) Comparison

30% MEA (Amine Absorption)	**-92** kJ/mol
PEBAX®:IL (SILM) [50:50]	**-13** kJ/mol [this study]



Conclusion

- Current literature suggests further testing of block copolymers in SILM fabrication may yield a decrease in permeability and selectivity tradeoffs
- 3% wt PEBAX® combines the benefits of polyamides and polyethers to create a stronger, more elastic, and thermally resistant SILMs.
- The SILMs sorption was most effective with PEBAX® 1657 at 10°C due to the balance of amorphous and crystalline blocks
- Block copolymers help to make SILMs more viable for industrial CO_2 capture.

Acknowledgements

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