Fifth Annual Conference on Carbon Capture & Sequestration

Steps Toward Deployment

Capture – Membranes (2)

Mechanical and Transport Behavior of Polybenzimidazole Dense Films Used for Elevated-Temperature Gas Separation

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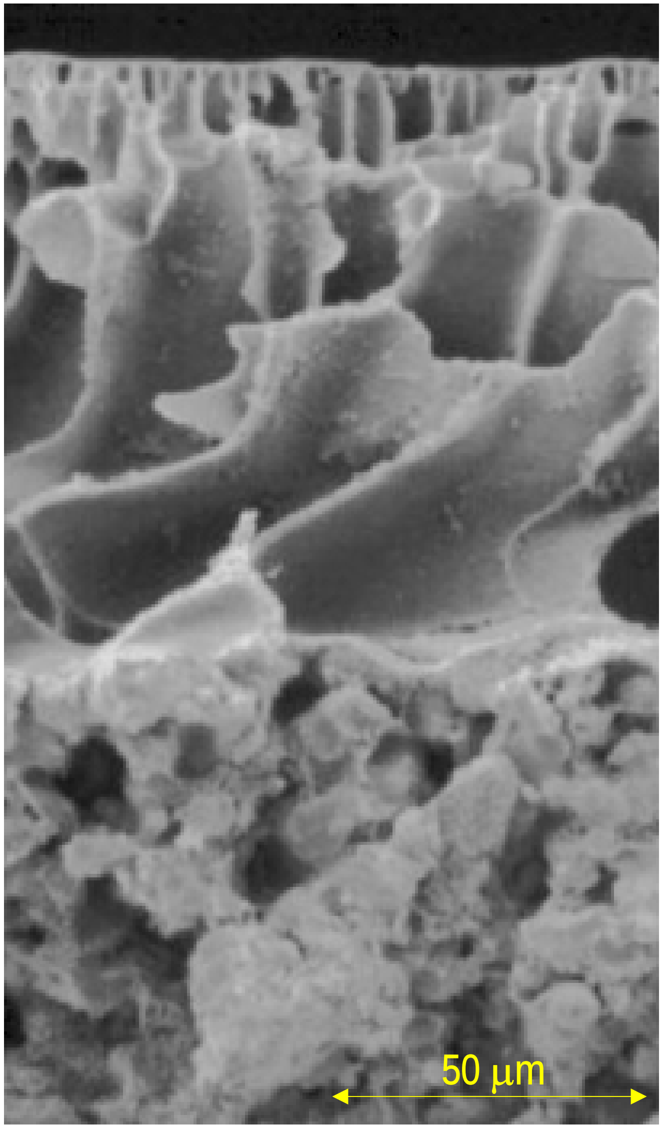
Overview

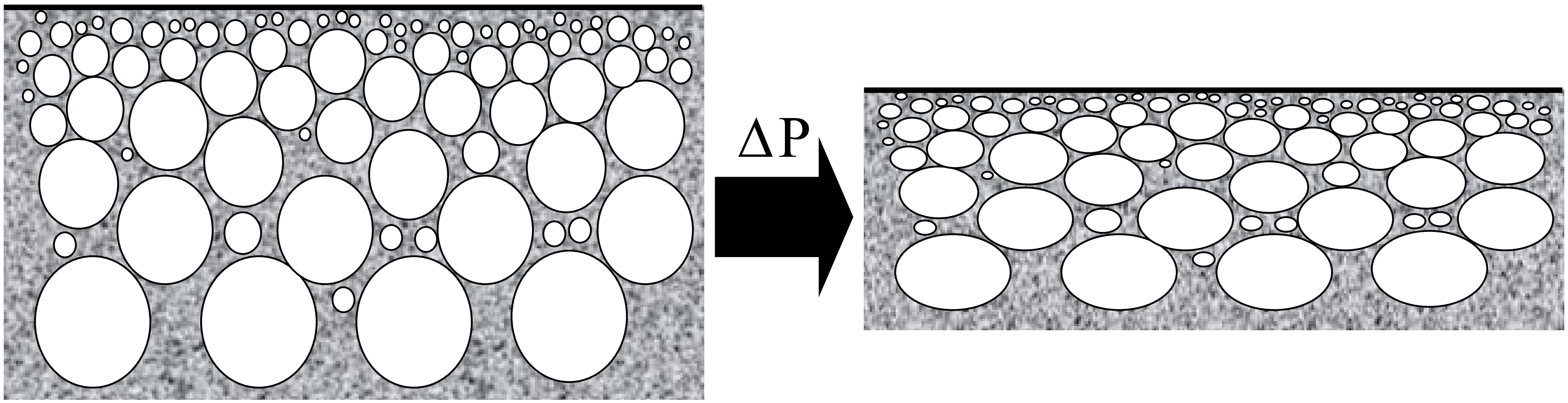


Asymmetric Polymer-Metallic Composite

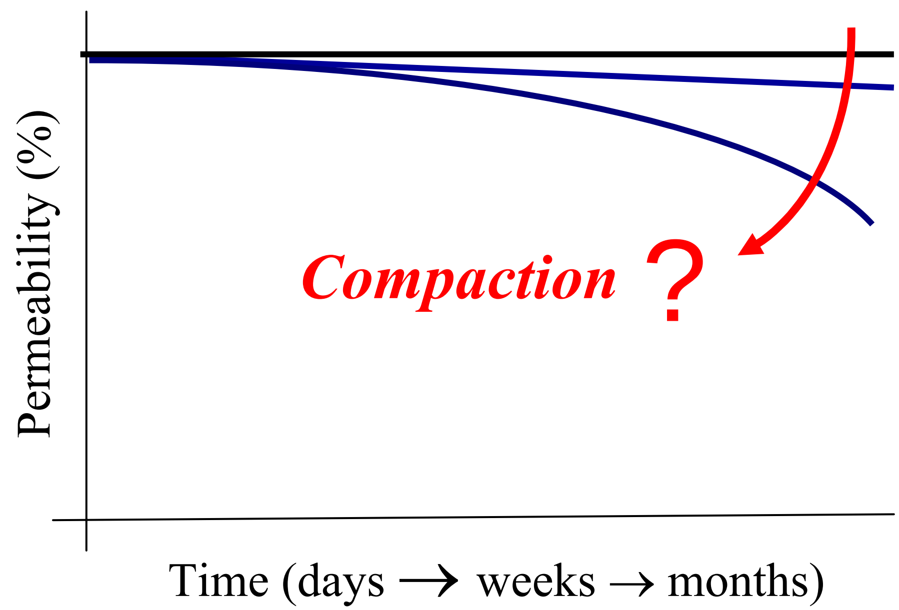
- **Background**
  - Compaction
  - Coupled Transport & Mechanical Responses
- **Materials & Methods**
  - Experimental Design
  - STAMP Apparatus
- **Results**
  - Strain & Permeability: N_2, CO_2 & He
  - Cycling tests
  - Diffraction & Thermal Analysis
- **Conclusions**

Background

- Compaction is the time-dependent compression, i.e. creep (strain), of the membrane structure that occurs under an applied trans-membrane pressure.



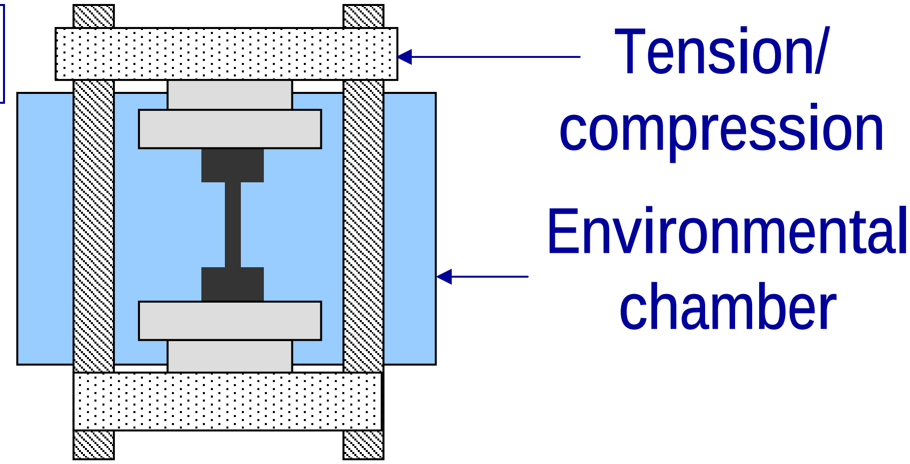
- Relatively few membrane compaction studies have been reported in the literature; most have utilized "off-line" mechanical tests and inferential evaluation to "show" that compaction contributes to flux decline during gas separation.



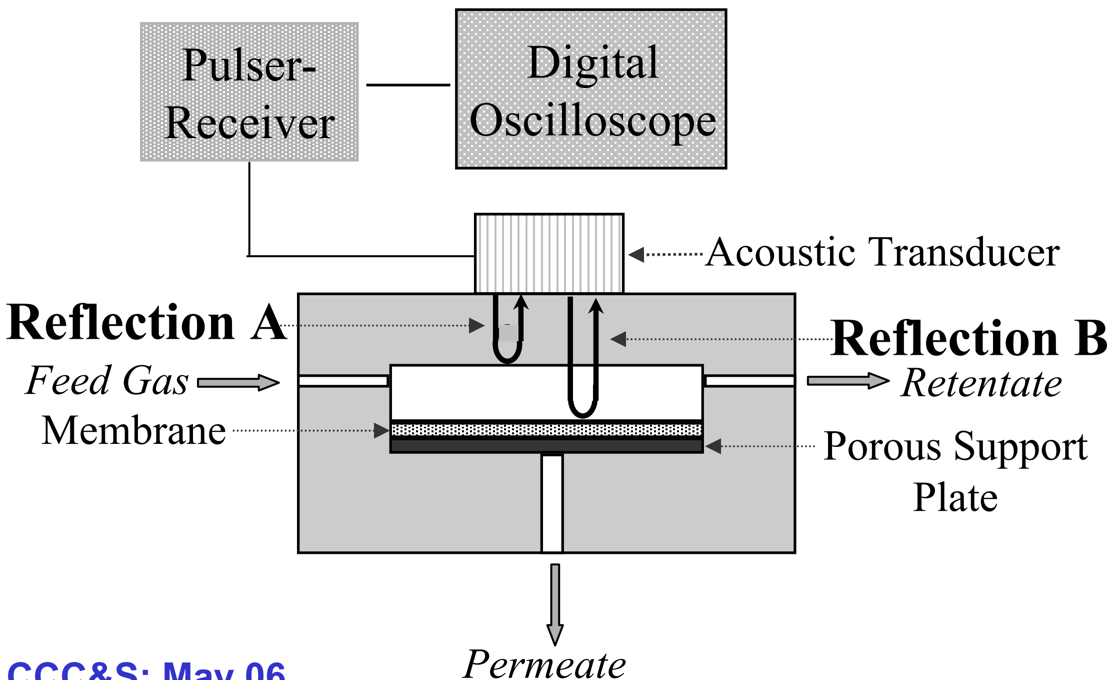
Background

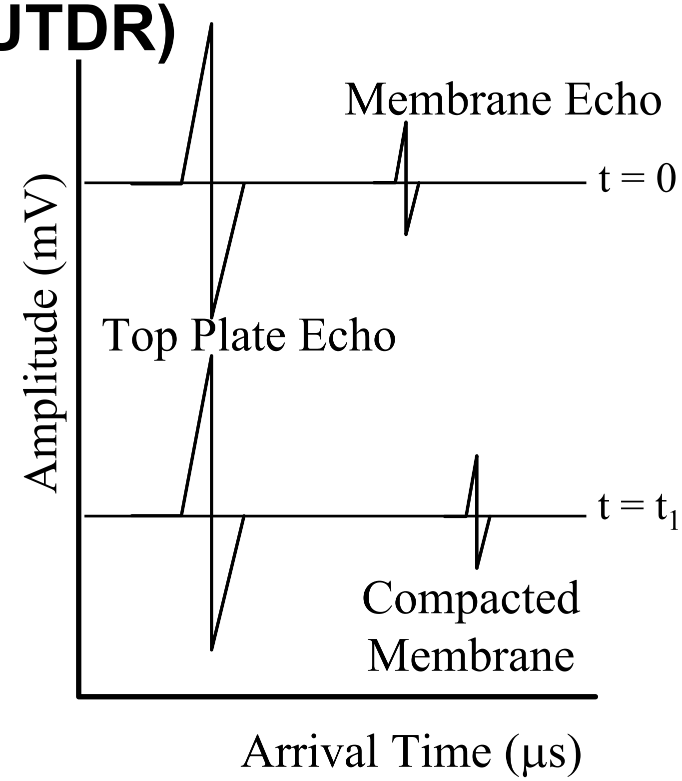
"Off-line" mechanical testing

- Testing conditions differ from those encountered during gas separation
- Compaction and permeation are not monitored simultaneously



Ultrasonic time-domain reflectometry (UTDR)





Background

- Elevated temperature separations offer significant thermodynamic and energetic advantages for many chemical processes; hence, a growing number of applications would significantly benefit from membranes that can operate at high temperatures in a chemically hostile environment.
- However, creep typically becomes more pronounced at elevated temperatures and may therefore accelerate any long-term decline in membrane performance.
- Elevated temperature compaction measurement provides an assessment of membrane performance under more realistic and industrially relevant gas separation conditions.
- Dense films studies represent a logical starting point for evaluating compaction and its effect on long-term gas transport; this information is important in our team development of polymer-metallic composite membranes for high-temperature gas-separation applications.

Materials and Methods

➢ *Materials*

- Polybenzimidazole (PBI): ~50-µm thick films; T_g ~ 450ºC

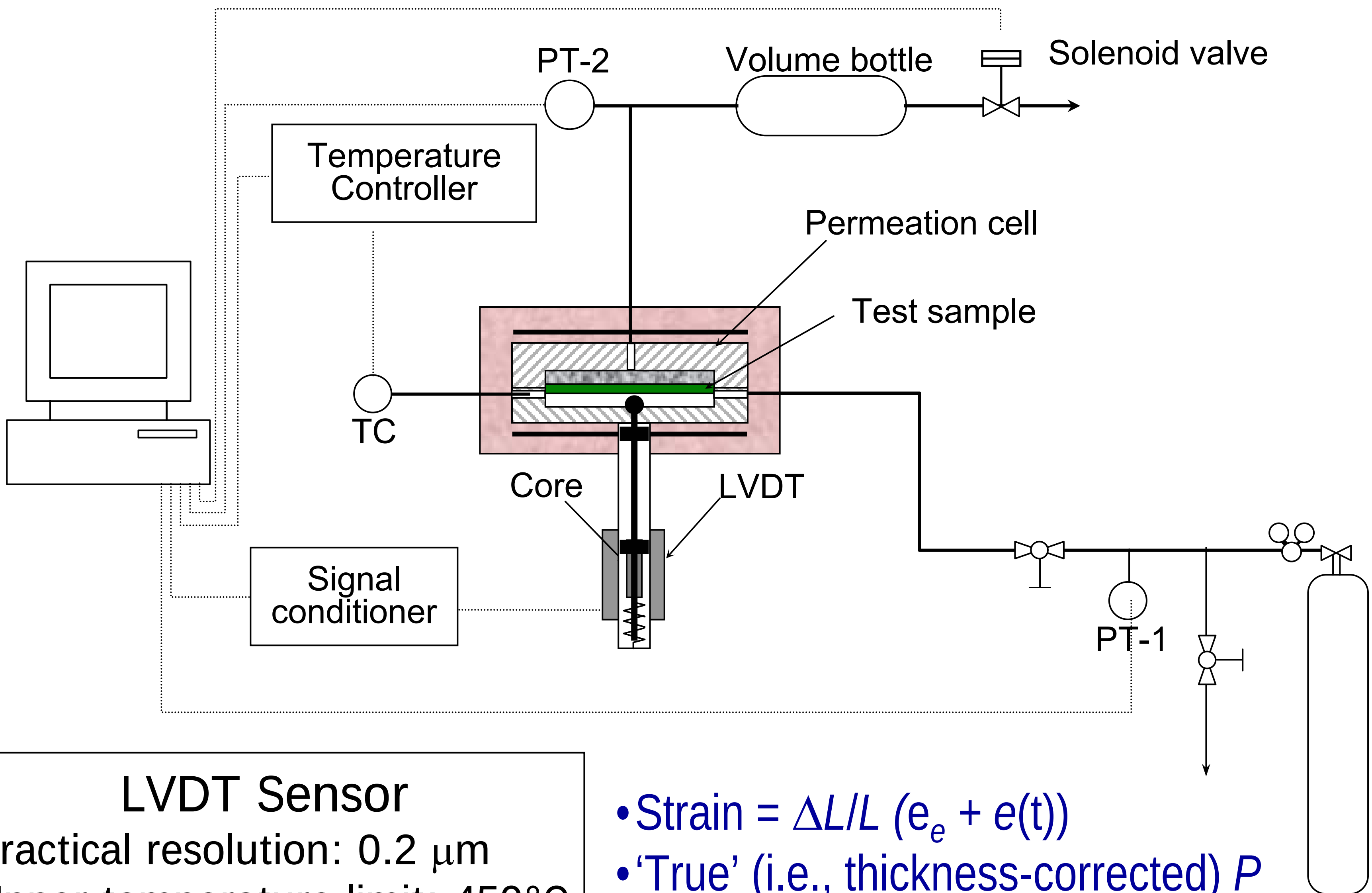
➢ *Experimental Design*

- Factorial design with replication
- Experimental variables: Temperature and gas medium
- Response variables: Compressive strain and permeability
- Control variable: Pressure (3.1 MPa)

➢ *Measurement Methodology*

- High Temperature Simultaneous Transport and Mechanical Property (STAMP) Measurement
- Independent characterization techniques including x-ray diffraction and thermal analysis (TGA)

STAMP Apparatus

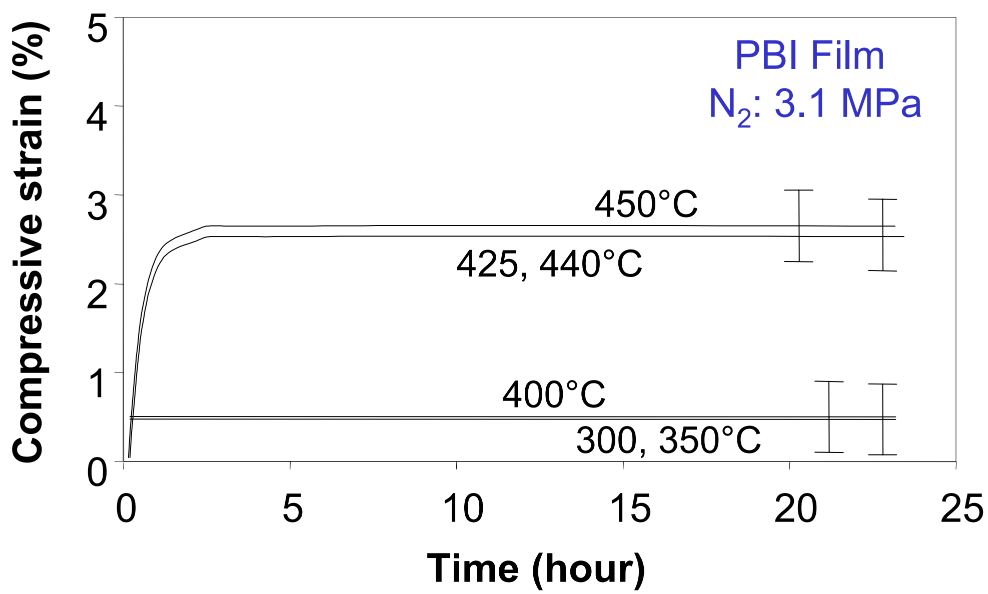


LVDT Sensor

- Practical resolution: 0.2 μm
- Upper temperature limit: 450°C

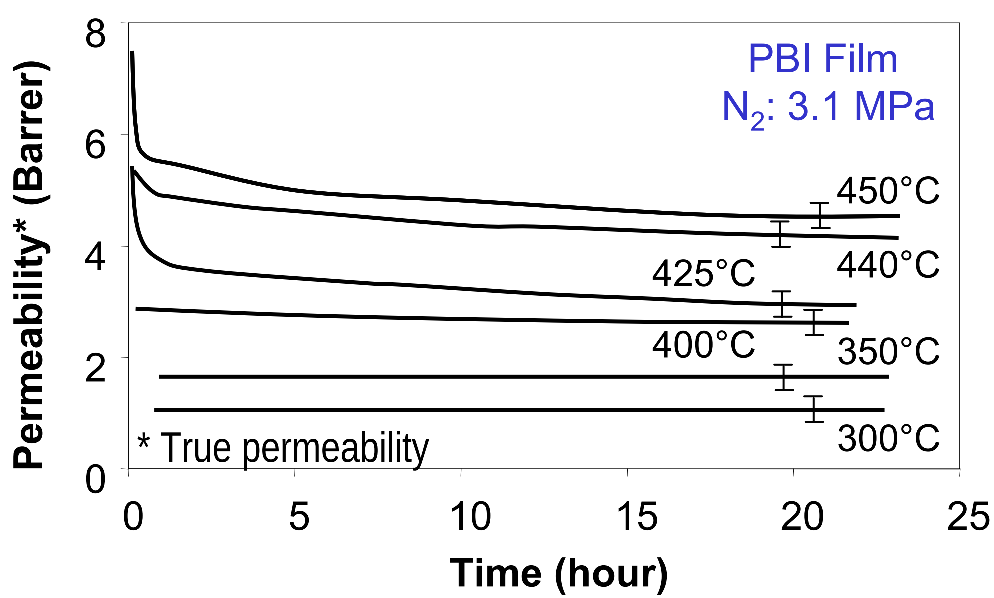
- Strain = $\Delta L/L$ (e_e + $e(t)$)
- 'True' (i.e., thickness-corrected) *P*

Strain/Permeability f(t,T): N_2



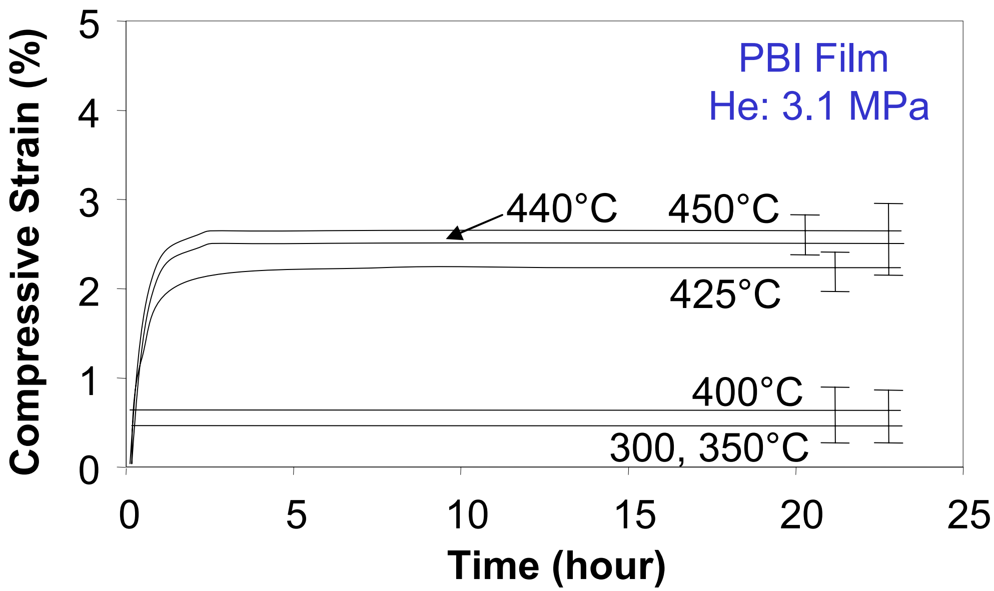
PBI films did not exhibit measurable creep strain below 400°C.

At higher temperatures, initial strain is observed but the response becomes asymptotic at ~2.5% after ~5 hours.

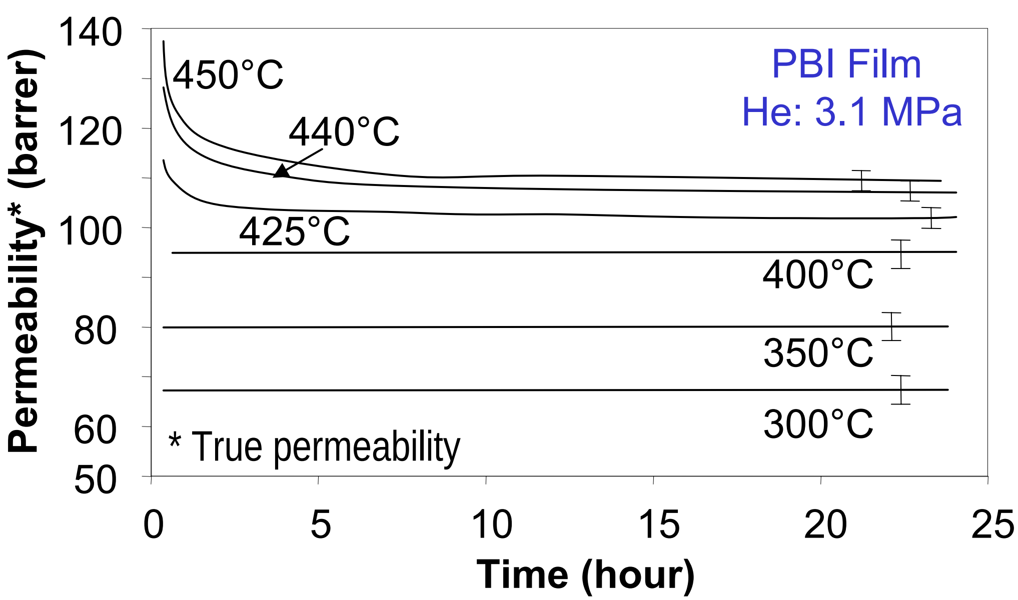


PBI films evidenced a time-dependent decrease in permeability at $T > 400°C$.

Strain/Permeability f(t,T): He

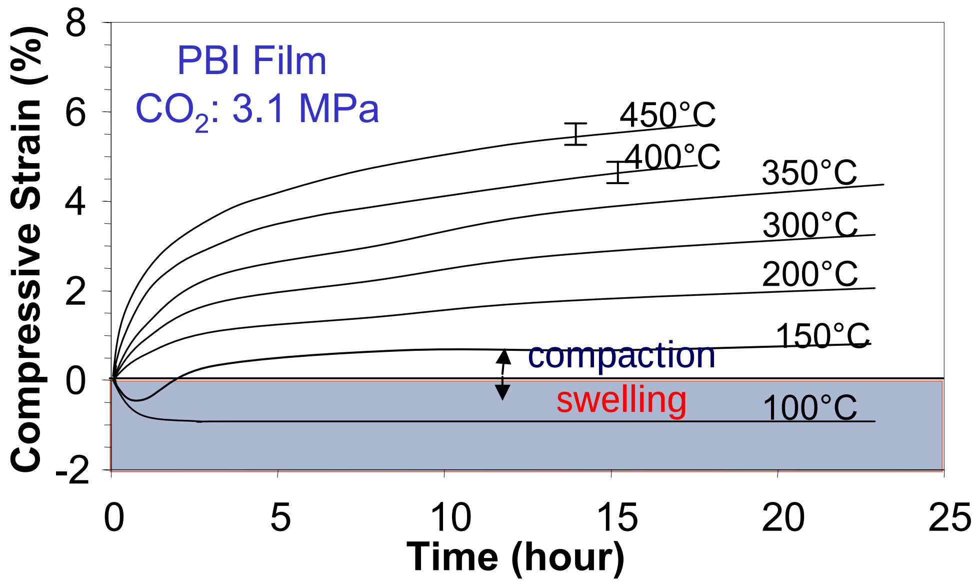


The strain response under helium is similar to that under nitrogen.

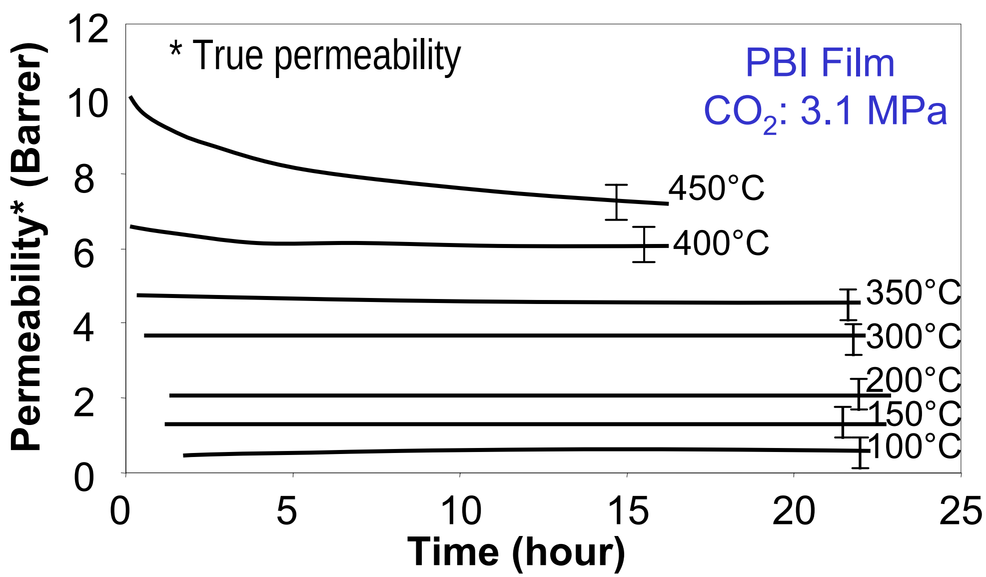


The overall helium time-temperature permeability trends are similar to those observed for nitrogen; however, permeability values for helium are more than an order of magnitude greater than those for nitrogen at the same temperature.

Strain/Permeability f(t,T): CO_2

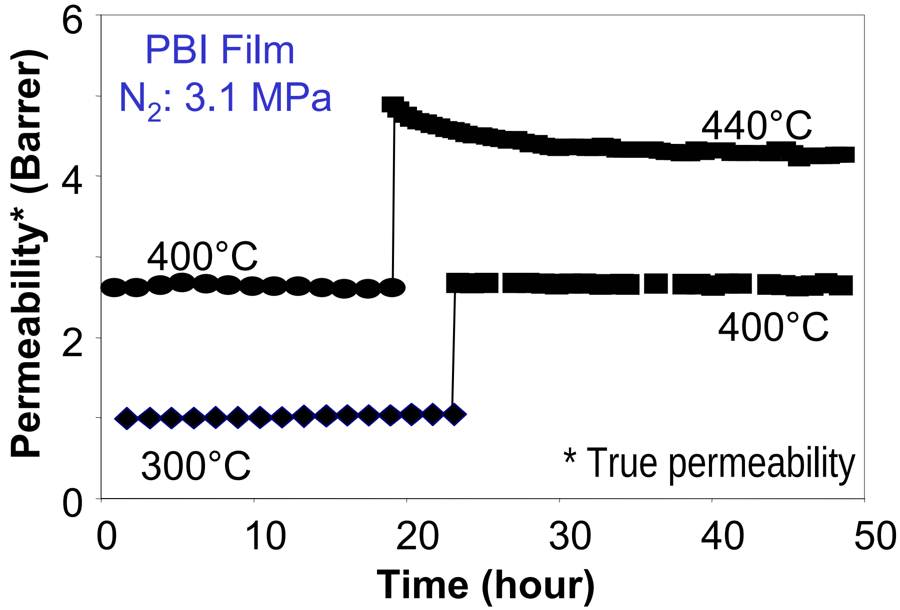


For $T < 200$°C, swelling is observed; for $T > 300$°C, appreciable creep occurs

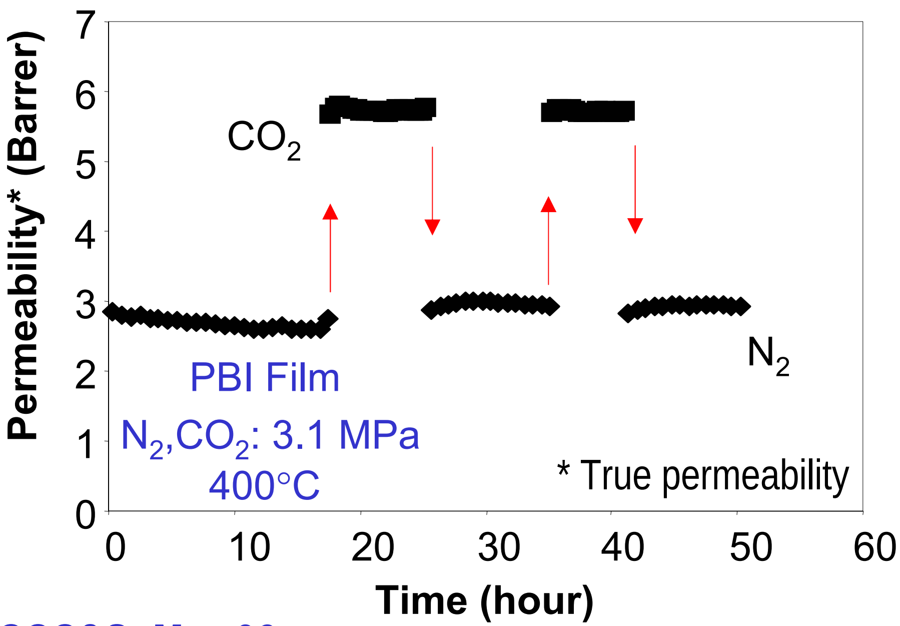


At 100°C, permeability increases slightly with time; at $T \geq 400$°C, permeability evidences a time-dependent decrease.

Cycling: Temperature & Gas



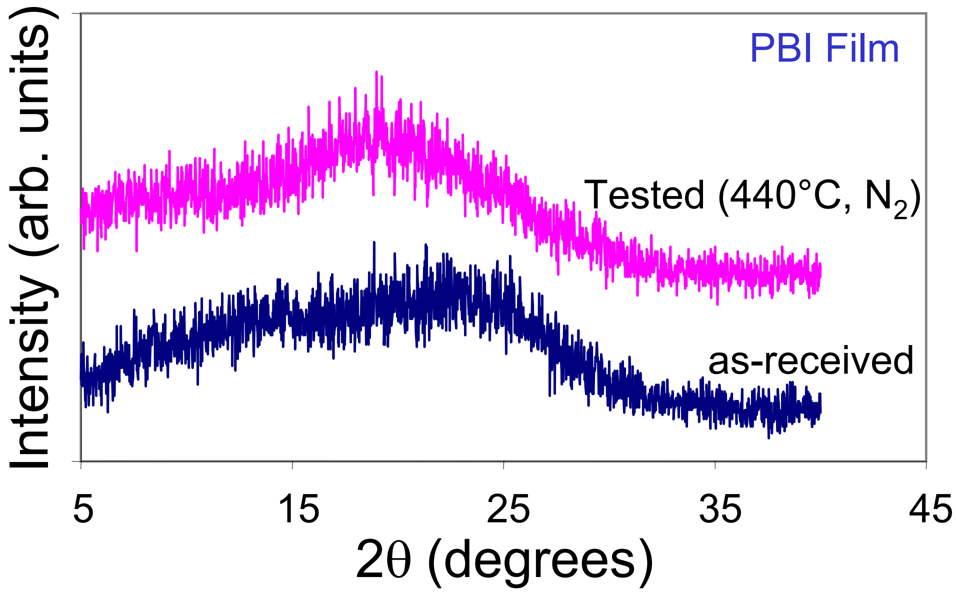
Time-dependent permeability values during temperature cycling show the same trend as those observed under isothermal testing.



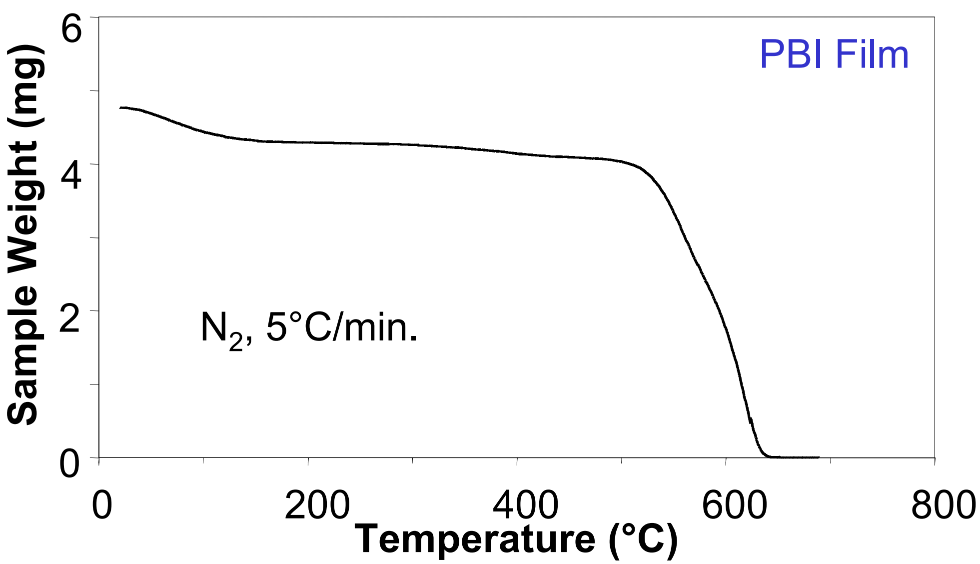
The permeability of PBI remains stable even when the test gas is cycled between inert (N_2) and plasticizing (CO_2).

Further, these values are comparable to those obtained from single-gas tests.

Results: XRD and TGA



X-ray diffraction profiles of PBI reveal amorphous halos; there is no evidence of strain-induced crystallinity during testing.



TGA results indicate a degradation temperature of ~ 500°C for PBI in N_2.

Conclusions

- Under N_2 and He, PBI dense films evidence relatively small creep strains; under CO_2, films showed swelling at lower temperatures and appreciable creep strain at higher temperatures, i.e. CO_2 is an effective plasticizer.
- For N_2, He and CO_2, PBI dense film permeability was stable for $T < \sim 400°C$ and decreased as a function of time for $T > 400°C$.
- The time scale for the observed changes in strain appears different than that for the corresponding changes in permeability.
- Initial changes in strain and permeability values at higher temperatures may be due to solvent and/or monomer loss.
- The protocol employed utilized short-term testing; hence, the issue of long-term permeability decline due to creep-induced microstructural changes requires further study.

Acknowledgement

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