Effect of hydration on the mechanical properties of anion exchange membranes

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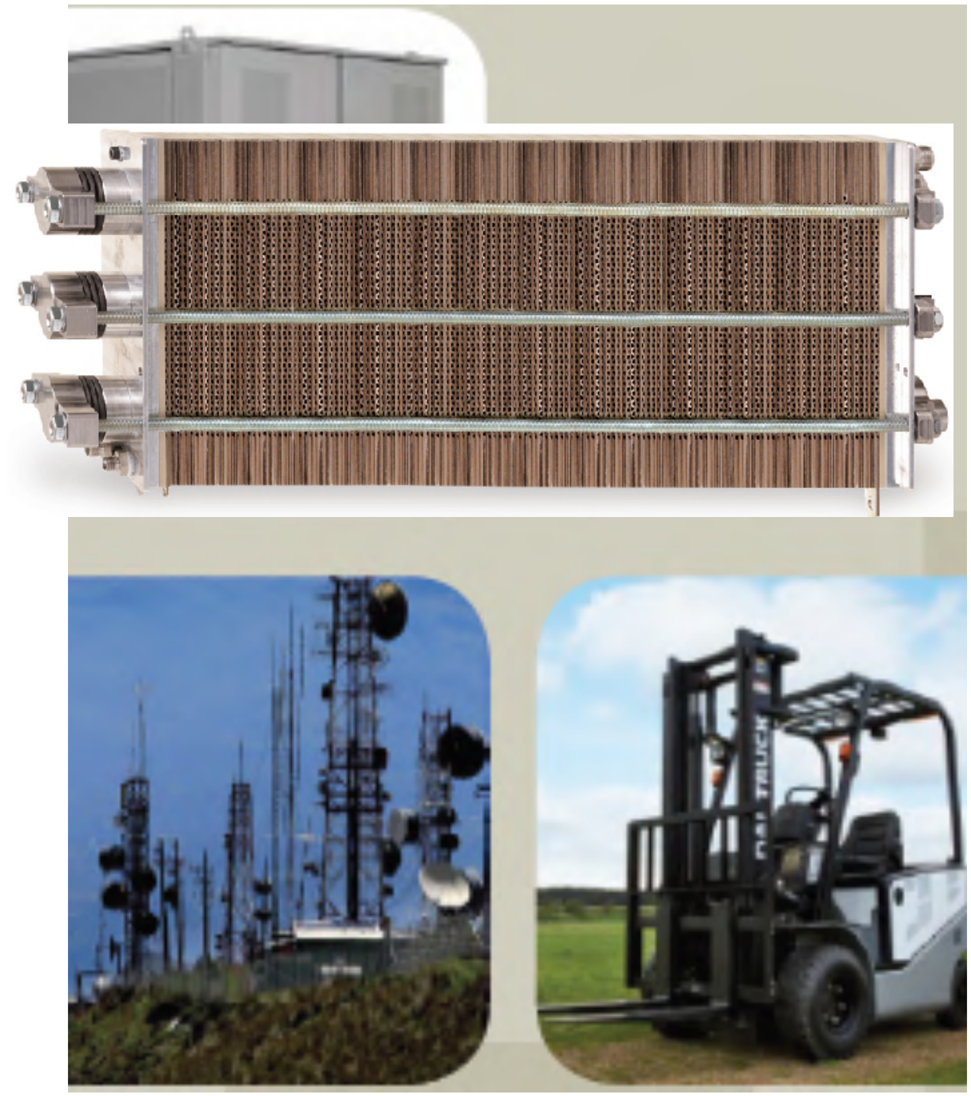
What is a fuel cell?

Electrochemical device with potential to provide low/ zero carbon emission power

- Grid back-up power
- Small portable devices
- Automobiles



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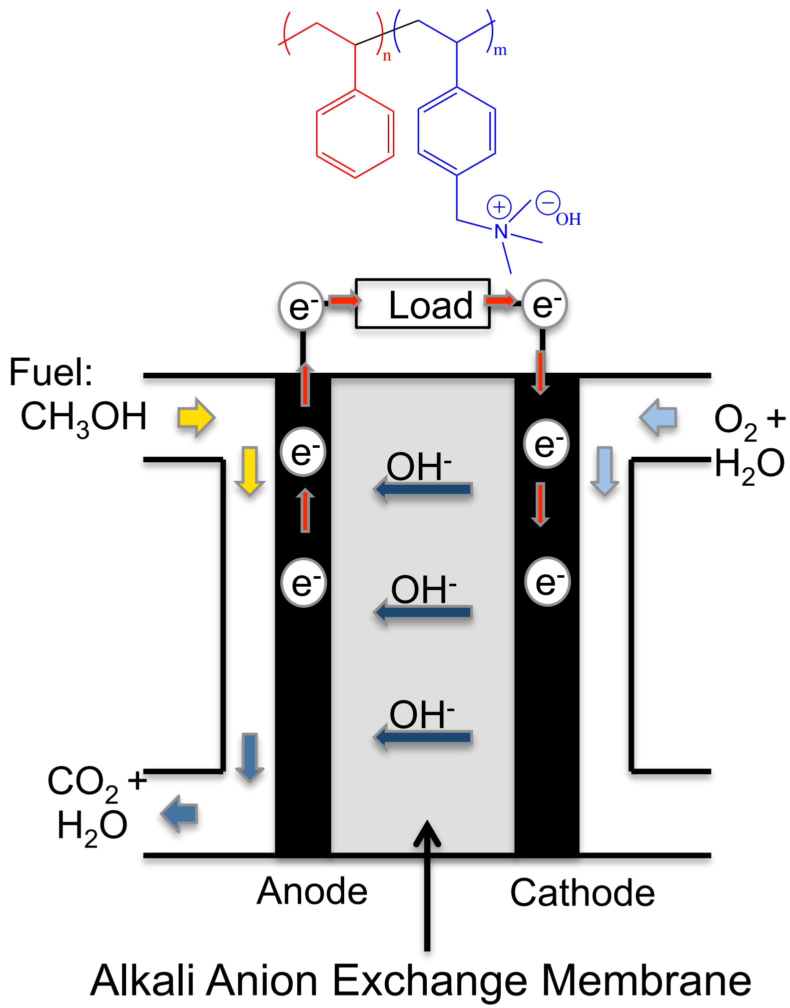
Anion Exchange Membranes (AEMs)

Solid polymer electrolyte membranes that transport anions in electrochemical devices



Advantages over PEMs:

Increased kinetics of alkali media

Non-Pt based catalysts

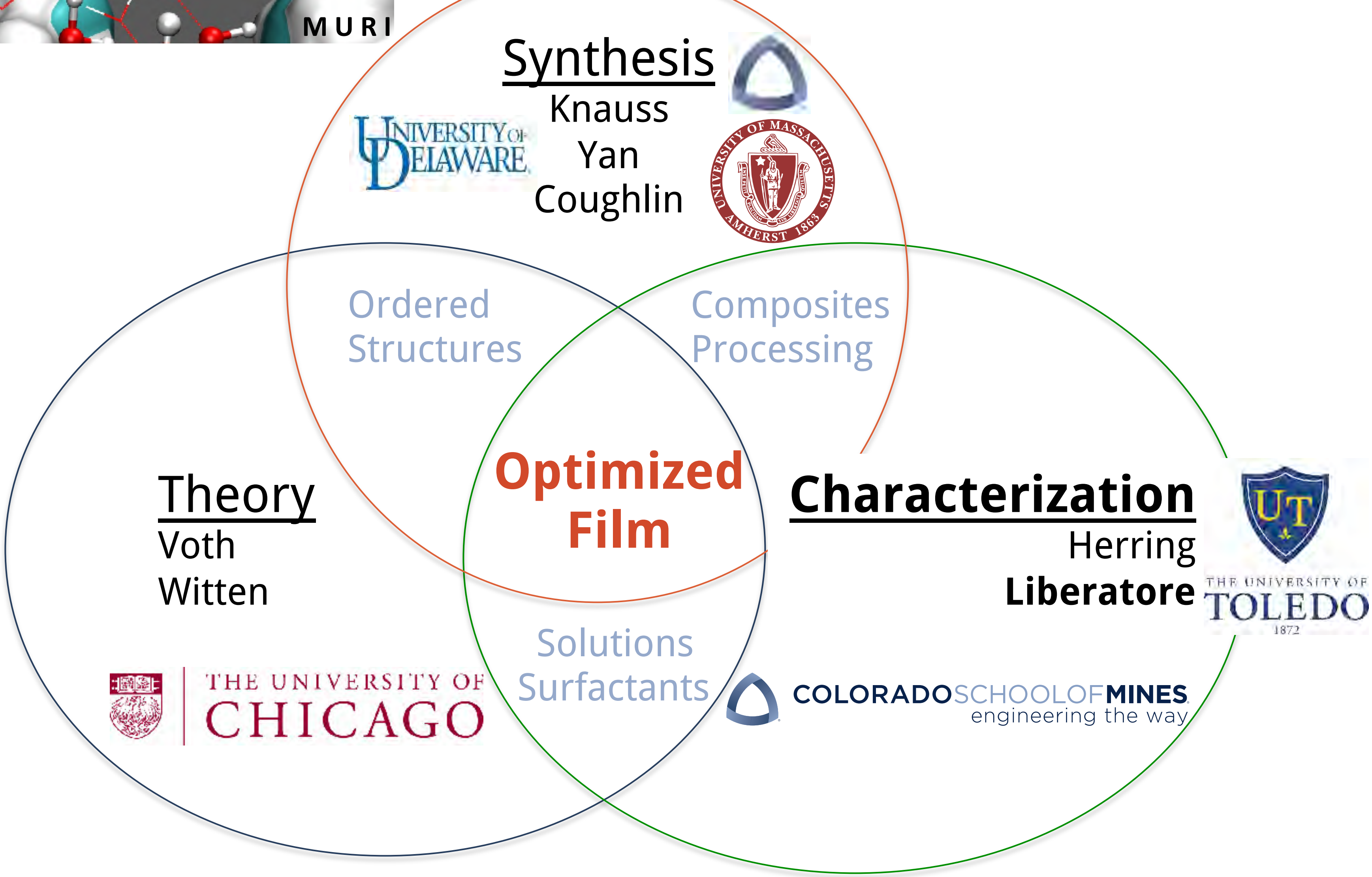
Reduction in methanol crossover

Challenges:

Lower ionic conductivity compared to PEMs

Chemical and mechanical stability

Collaboration for robust AEM



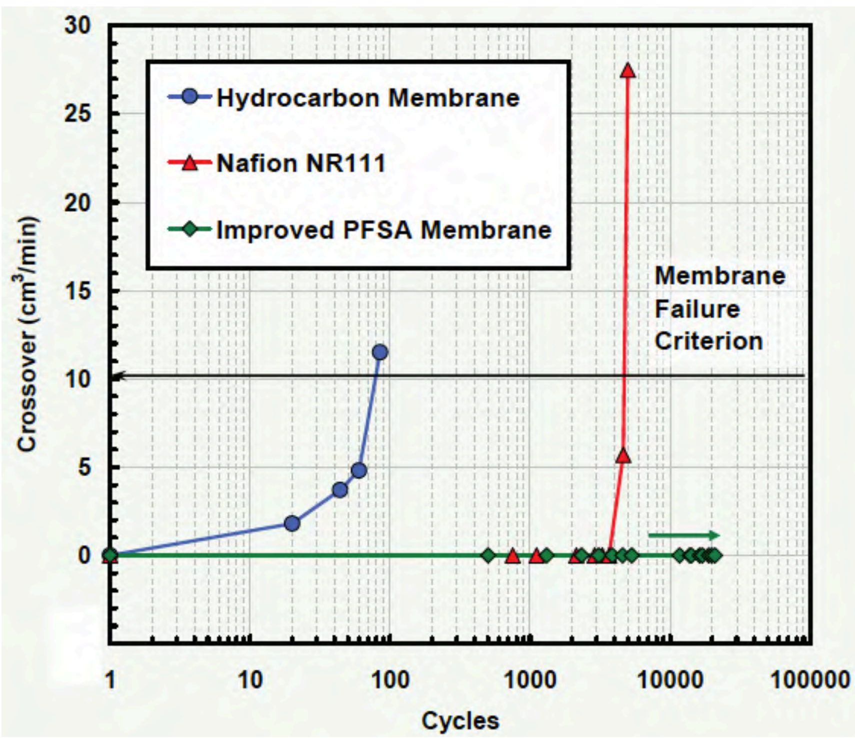
Requirements of an AEM

1. **High ionic (OH^-) conductivity**
   - Thin membranes, to reduce ionic resistance
2. Selective permeability to transport ions and prevent fuel/air crossover
3. **Adequate water sorption without significant dimensional swelling**
4. Chemical stability (backbone and ionic site)
5. **Mechanical stability**
   - Durable and thin membranes

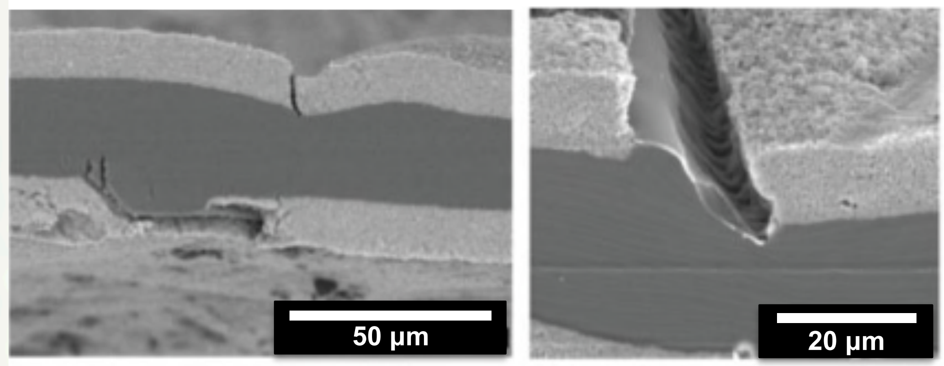
Film durability critical for device lifetime

Variations in humidity can lead to failure

Quantify the interplay of swelling and mechanical performance



Mathias et al., *Electrochemical Society Interface* **14** (2005).



(a) Nafion® NR111 (b) Nafion® NR111

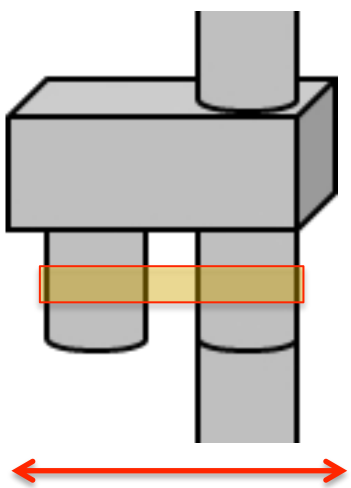
Patankar et al., *J. Polym Sci, Poly Phys.*, **48**, (2010)

Mechanical testing w/ controlled RH

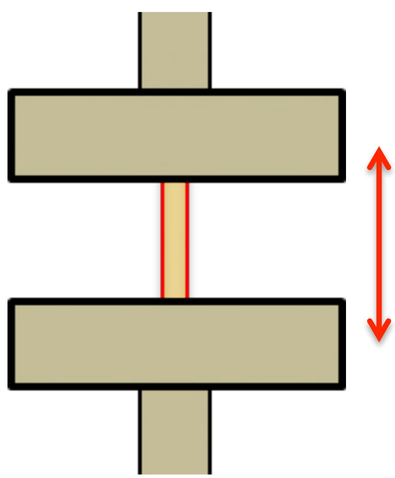
TA ARES rheometer with SER fixture for extensional tests and film/fiber tension fixture for DMA

Small sample size 20 mm (L) X 5 mm (W)

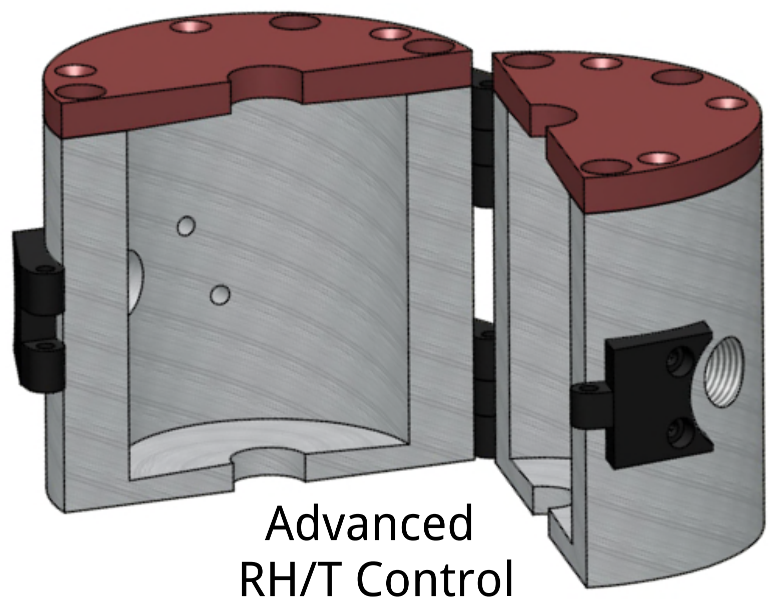
Custom sample chamber to control temperature/humidity



(SER) Elongation and Tensile



DMA



Advanced RH/T Control Oven

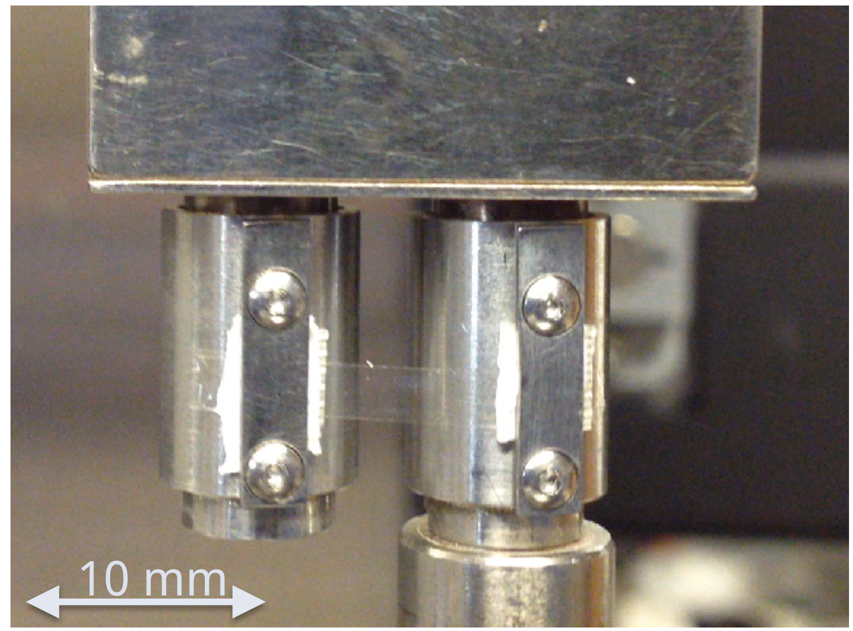
Benchmarked with LDPE and Nafion

Modified SER for thin film testing

Screw down clamps with silicone rubber holds film securely in place

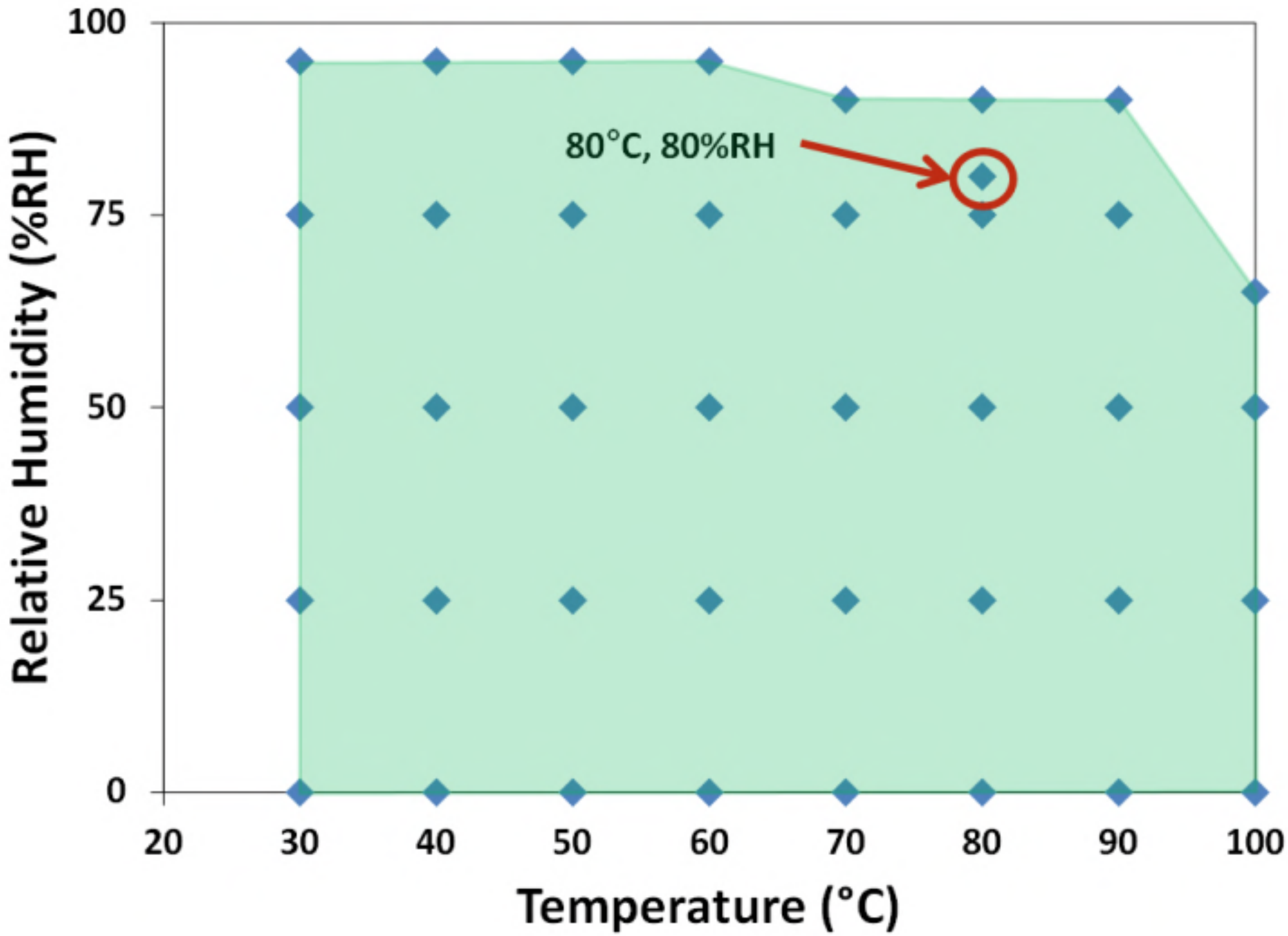
Testing below the melting temperature

Characterizes
10-100 micron thick films



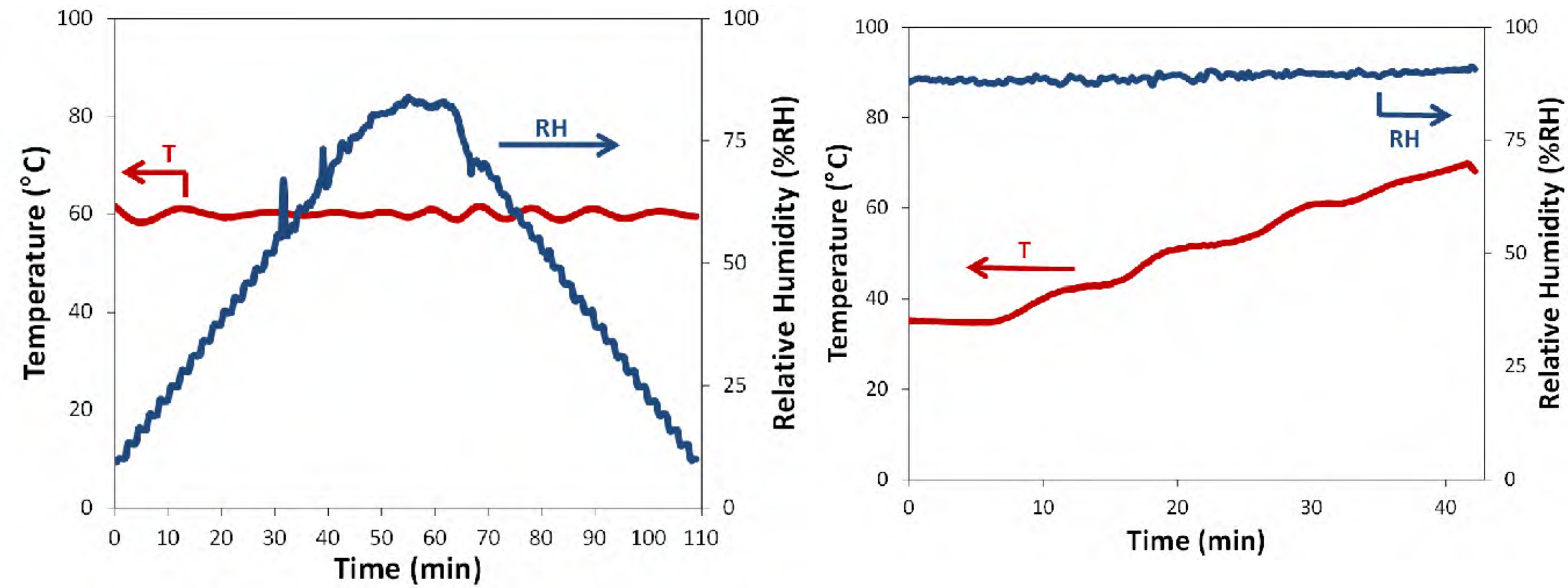
SER <5% of material needed for tensile tester

T & RH conditions available



Temperatures up to 150°C

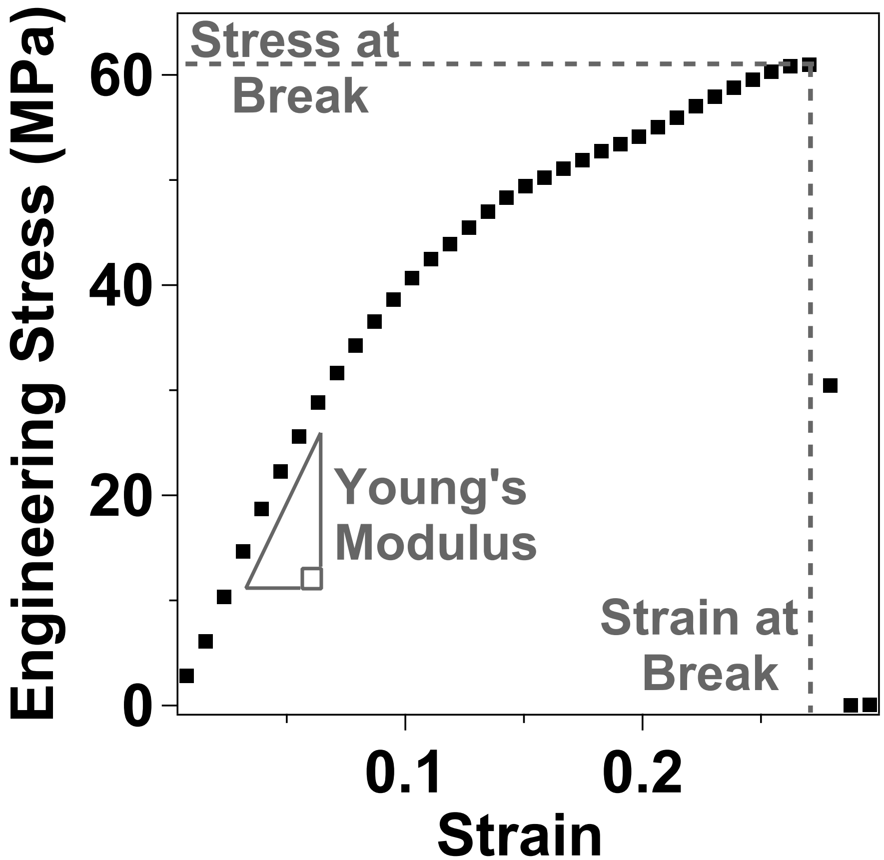
Ramping T or RH



Investigate transitions as function of water content

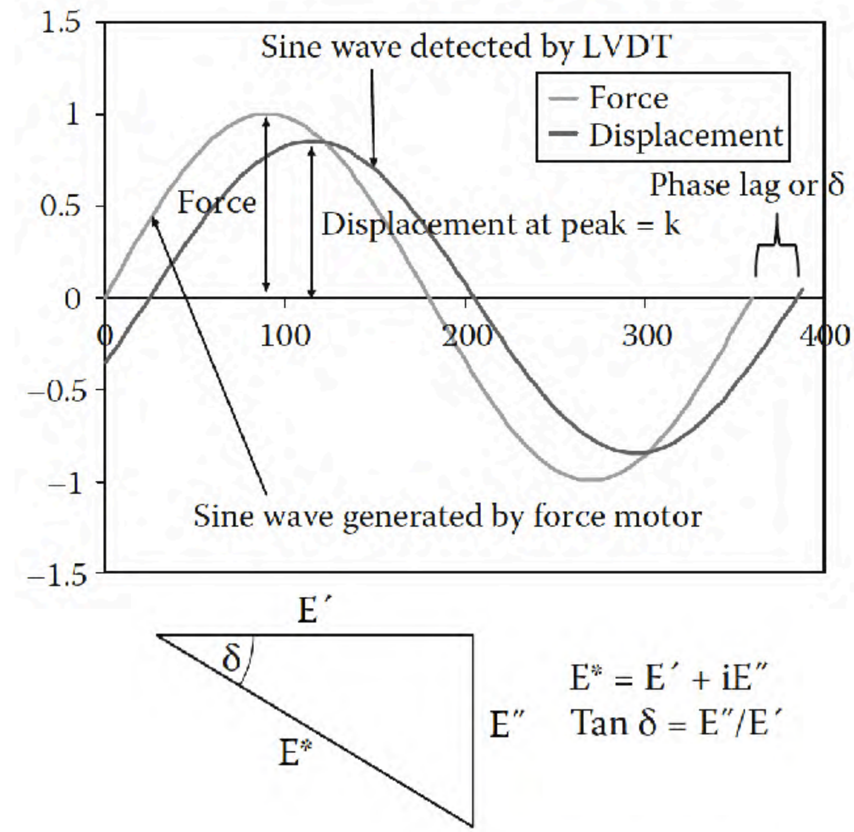
Two mechanical tests

Extensional Testing



Young’s Modulus (Elasticity)
Stress at Break (Strength)
Strain at Break (Elongation)

Dynamic Mechanical Analysis



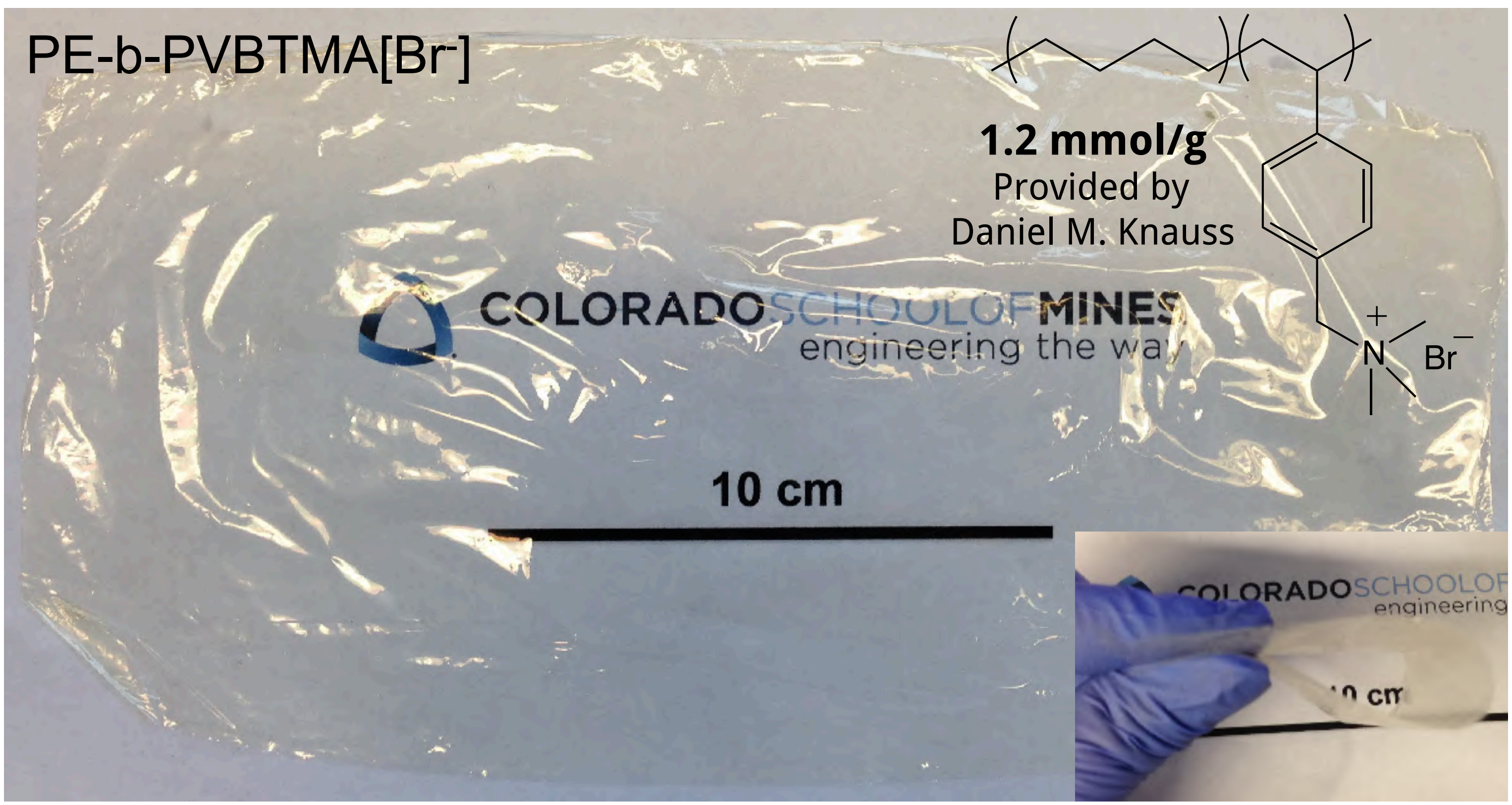
E* – Complex Modulus
E’ – Elastic component (Stiffness)
E” – Viscous component (Energy Loss)

Menard, K.P., Dynamic Mechanical Analysis, A Practical Introduction, 2nd ed., CRC Press, Inc., Boca Raton 2008.

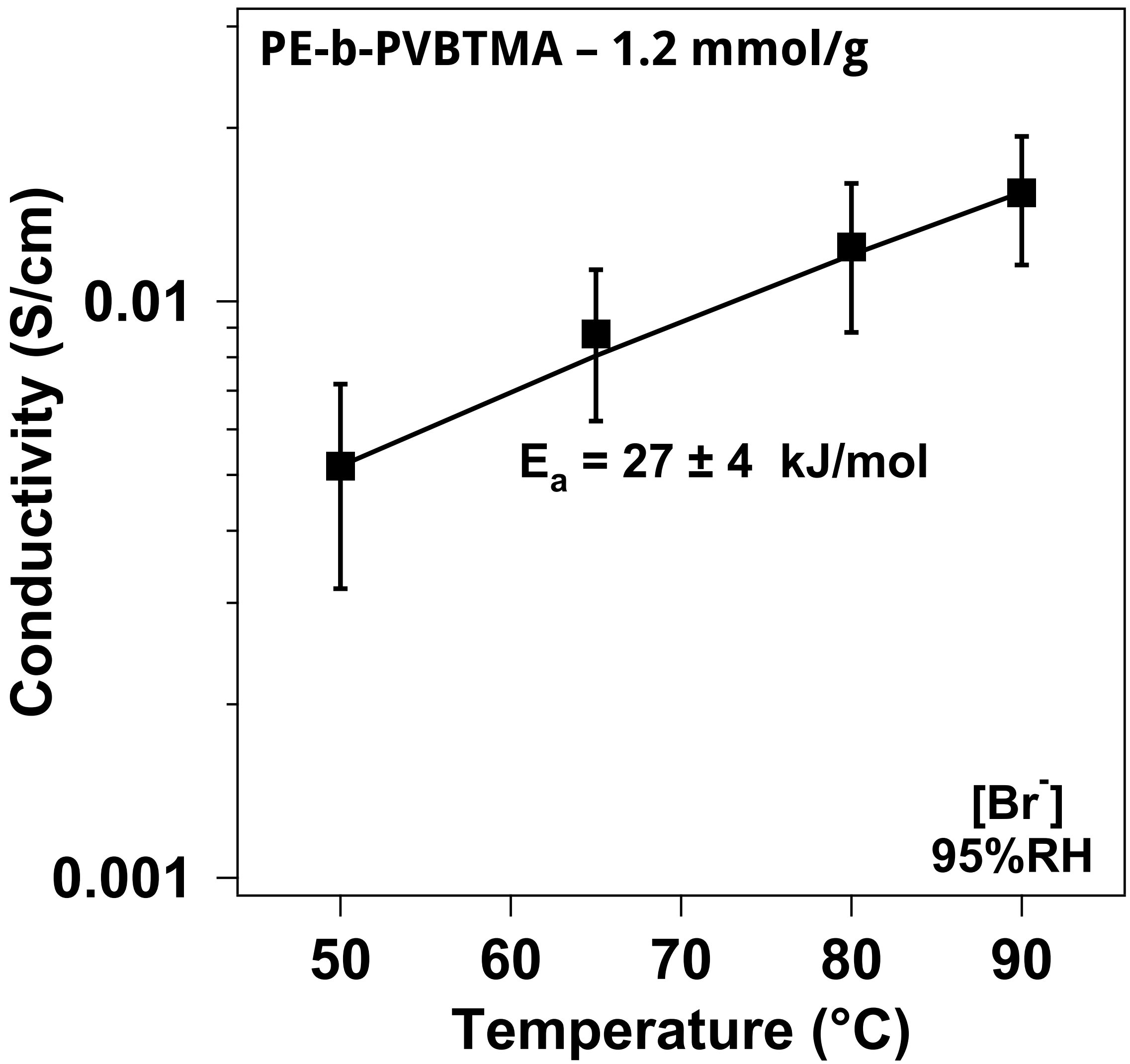
Robust, conductive, and thin AEM

Rubbery, polyethylene based, diblock to improve elasticity and flexibility

Solution casting large (300 cm^2), uniform 10 μm films



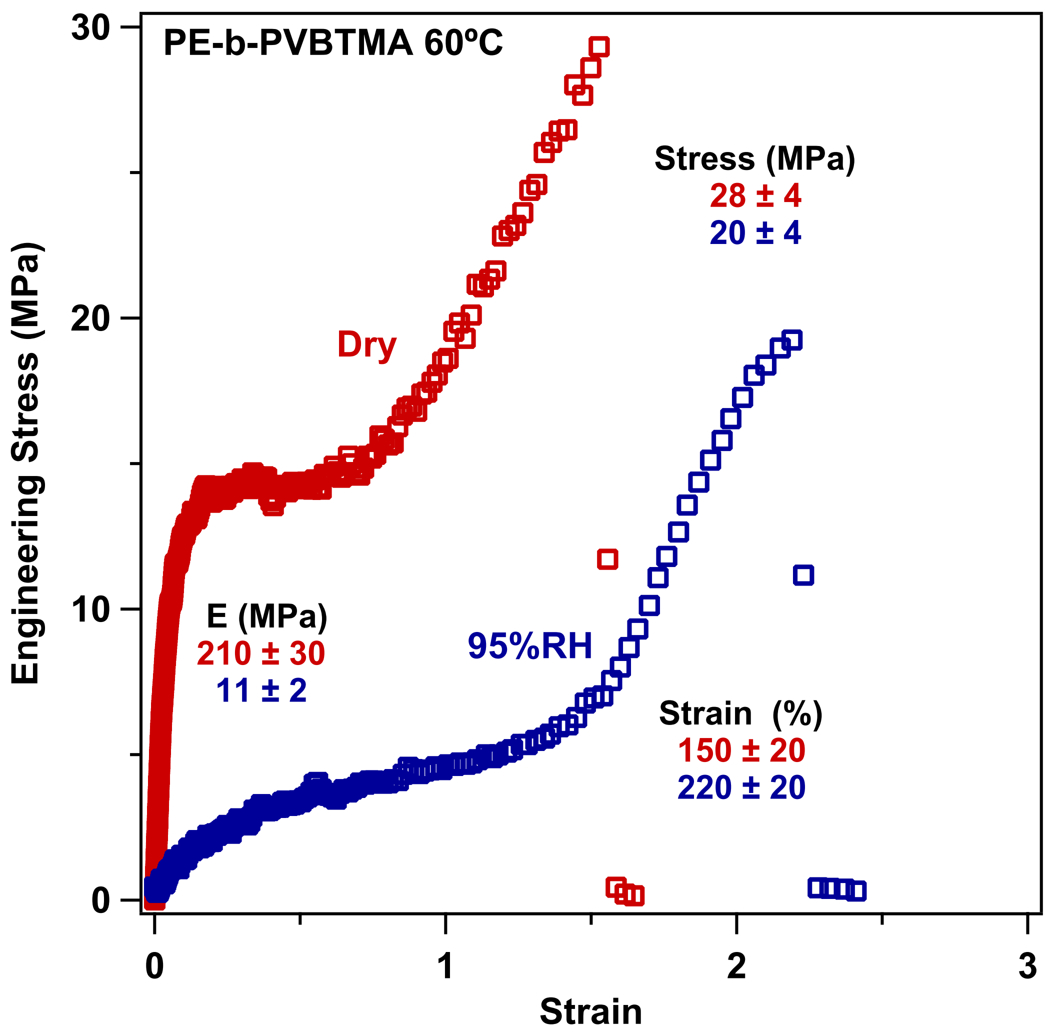
PE diblock is conductive



PE Diblock has modest conductivity, given lower IEC

Minimal dimensional swelling from water = 8 ± 3%

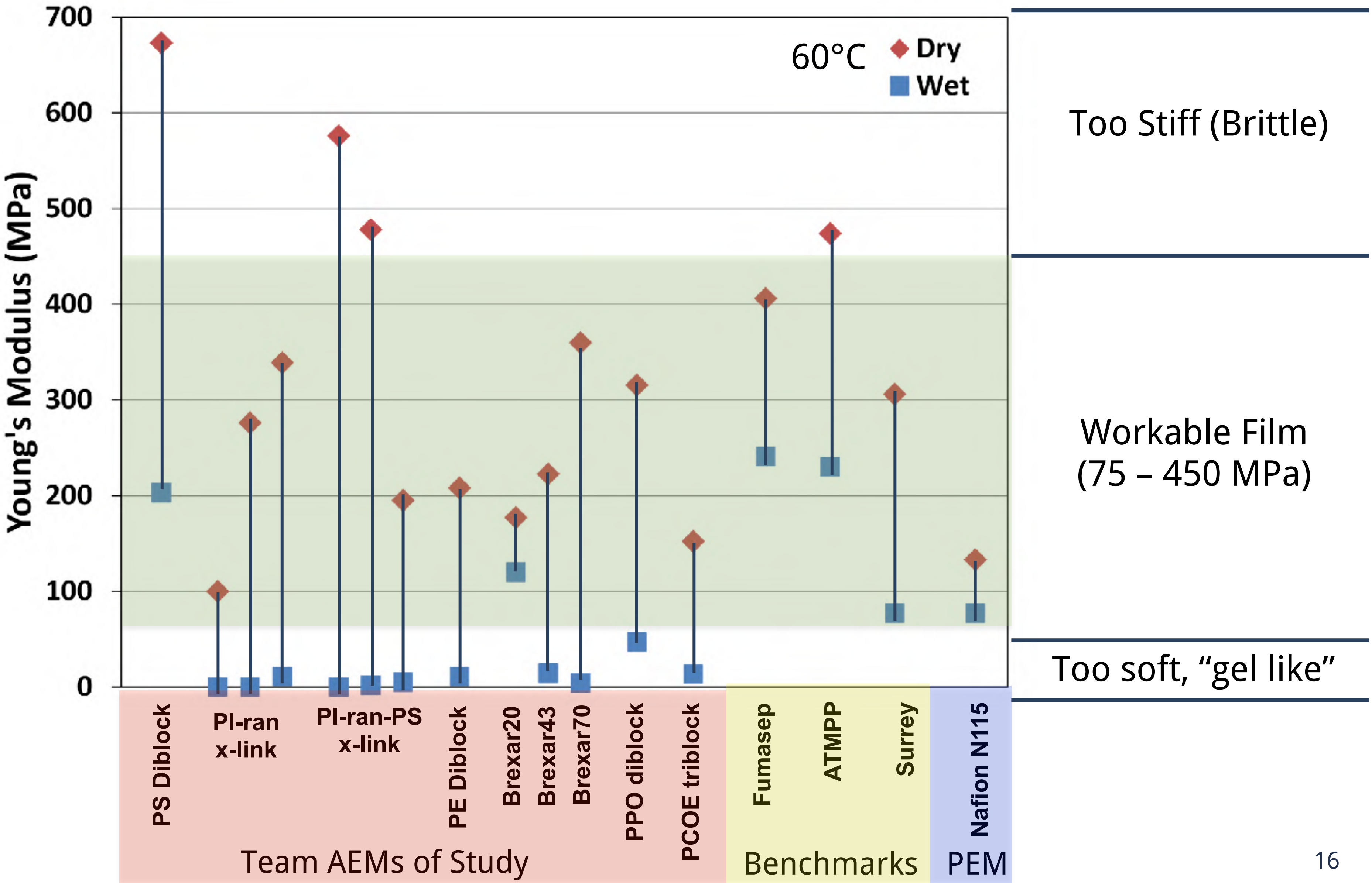
PE diblock has “good” properties



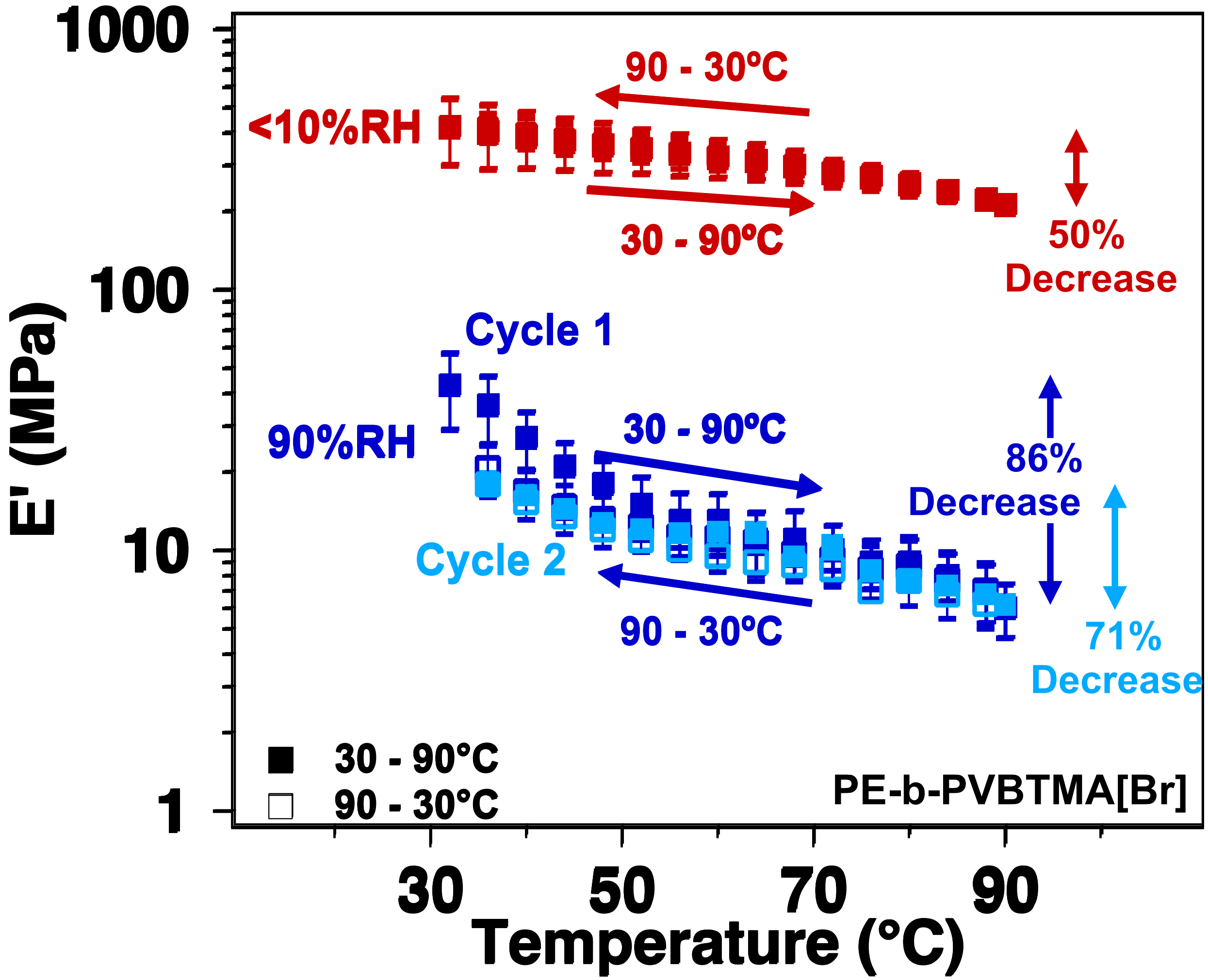
Good strength & elasticity at dry conditions

At hydrated conditions films soften significantly

Wanted: Moderate elasticity dry & wet

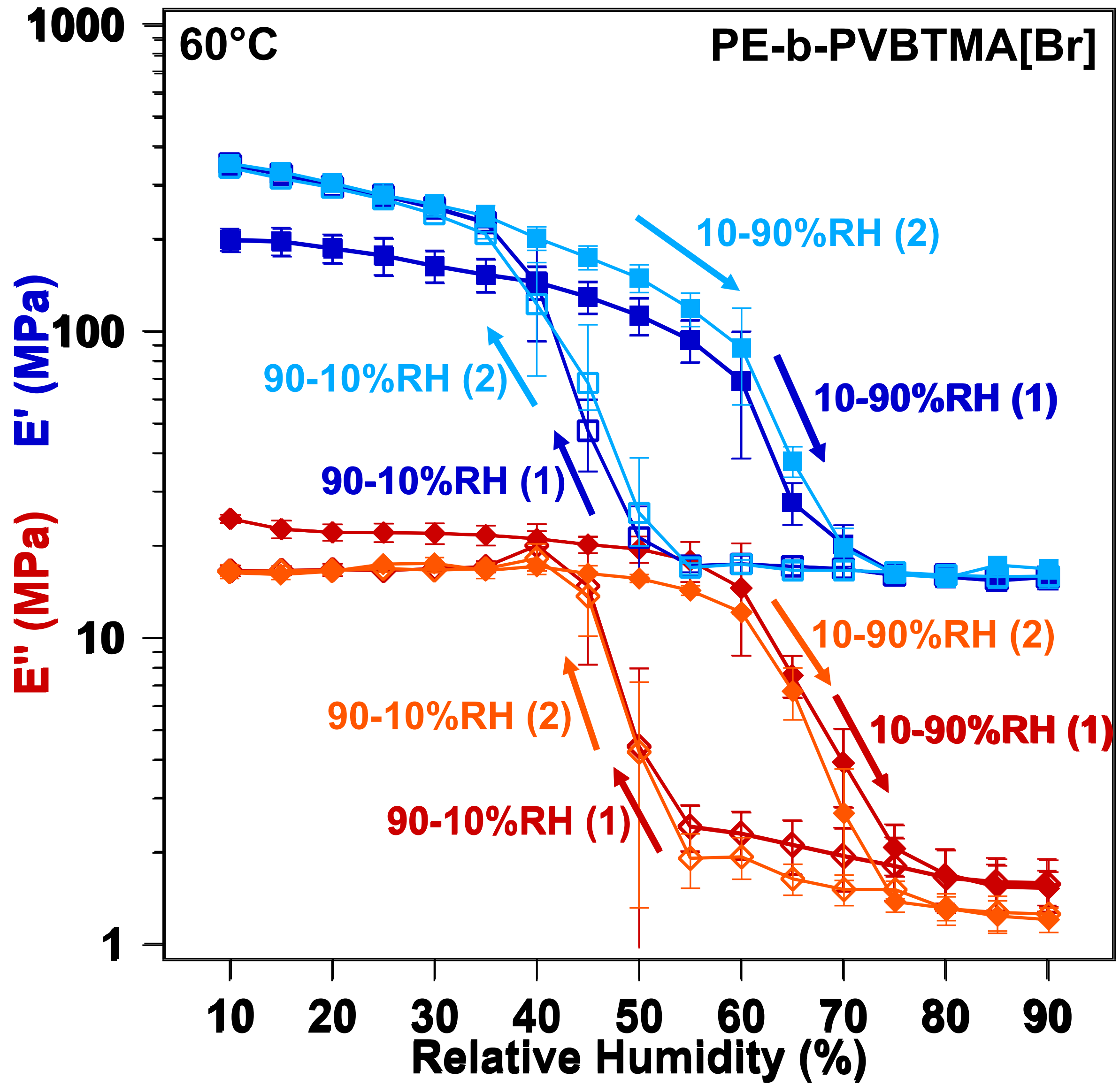


Dynamic thermomechanical response



Difference between dry/hydrated states warranted testing at intermediate humidities

Dynamic hygromechanical response

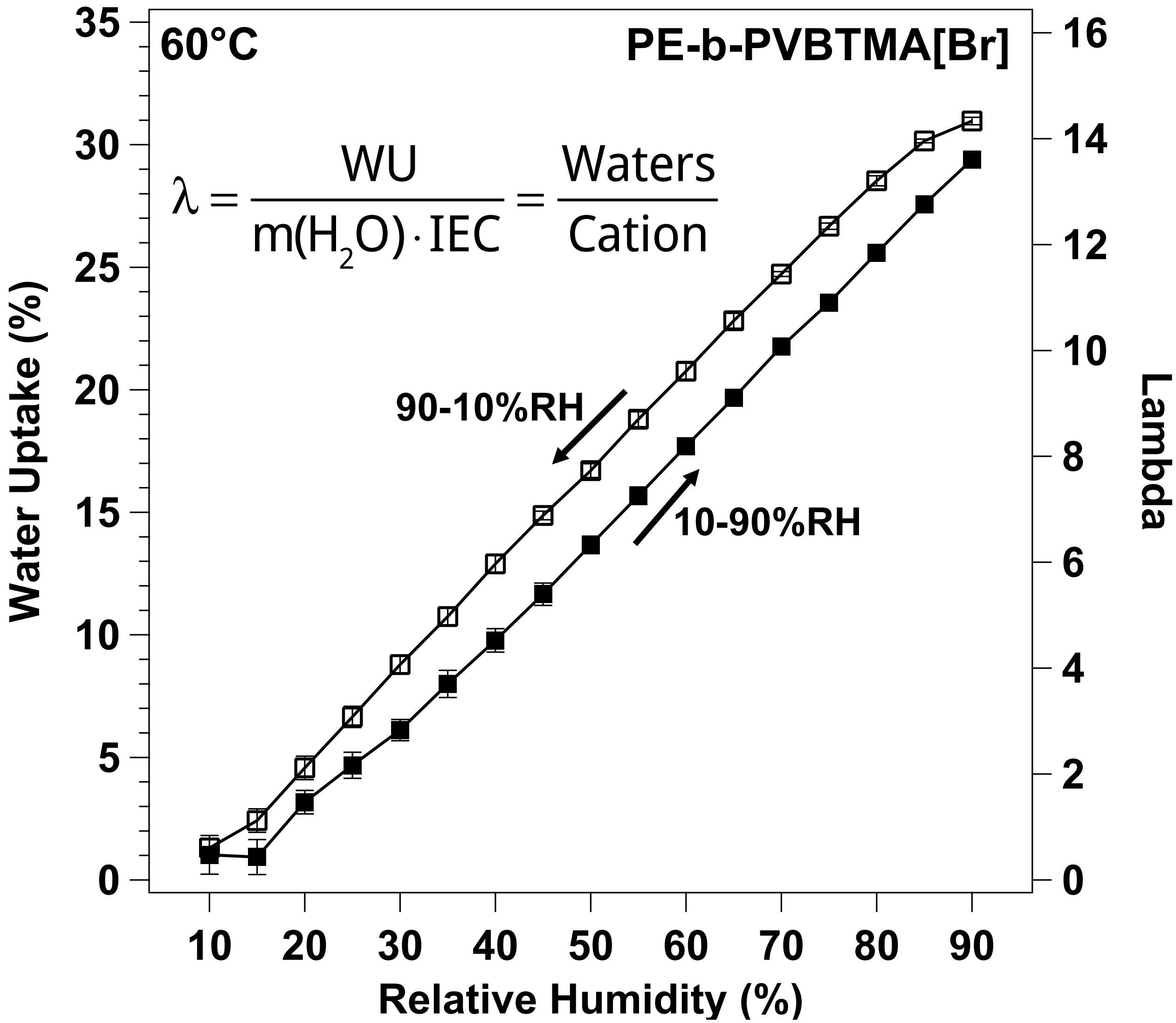


Humidification causes sharp softening transition at ~65%RH

Transition is reversible, but displays hysteresis

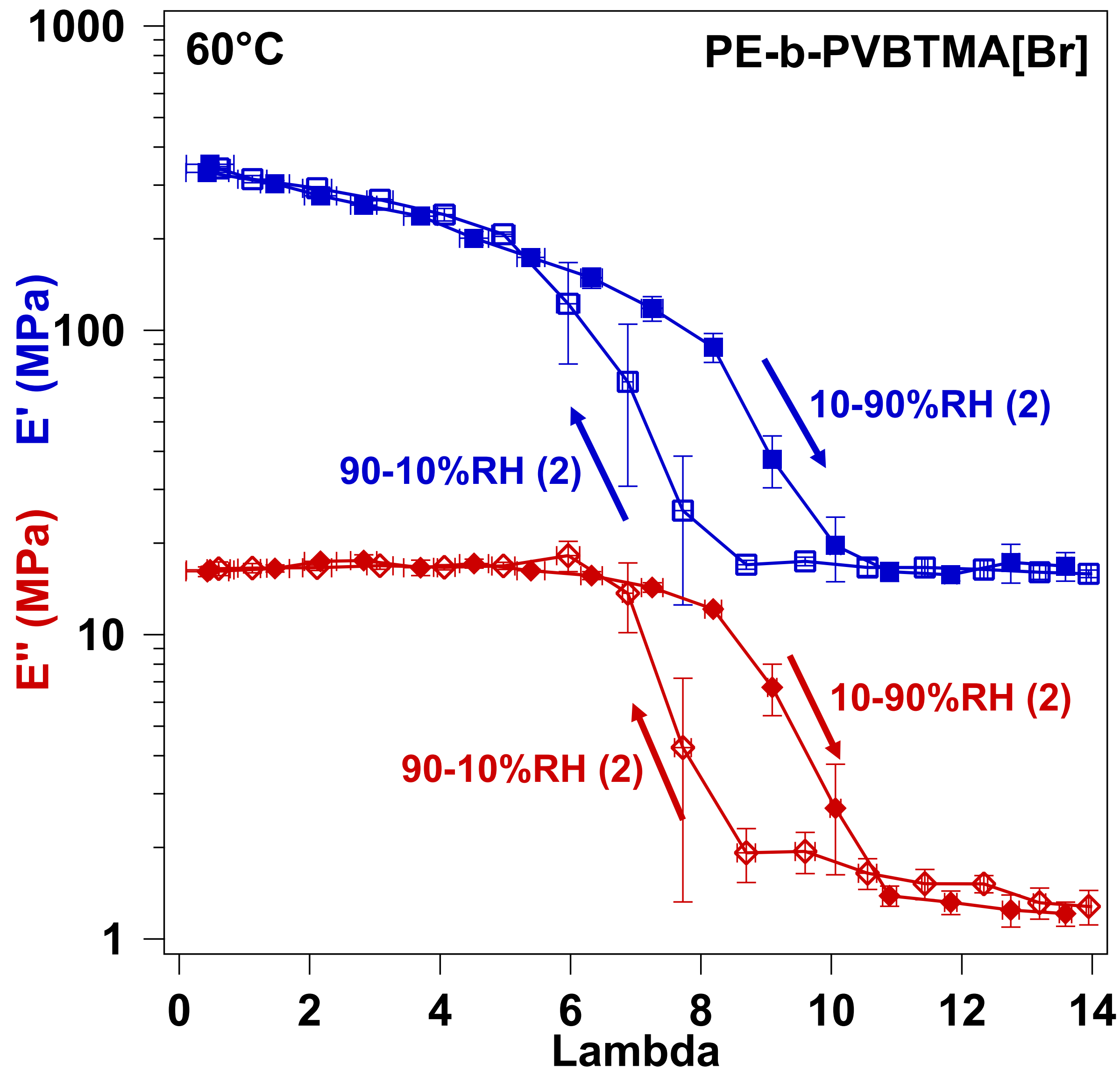
Restiffening during dehumidification ~45%RH

Water content varies with humidity



- Slight hysteresis between sorption and desorption
- DMA can be normalized to lambda to account for water content

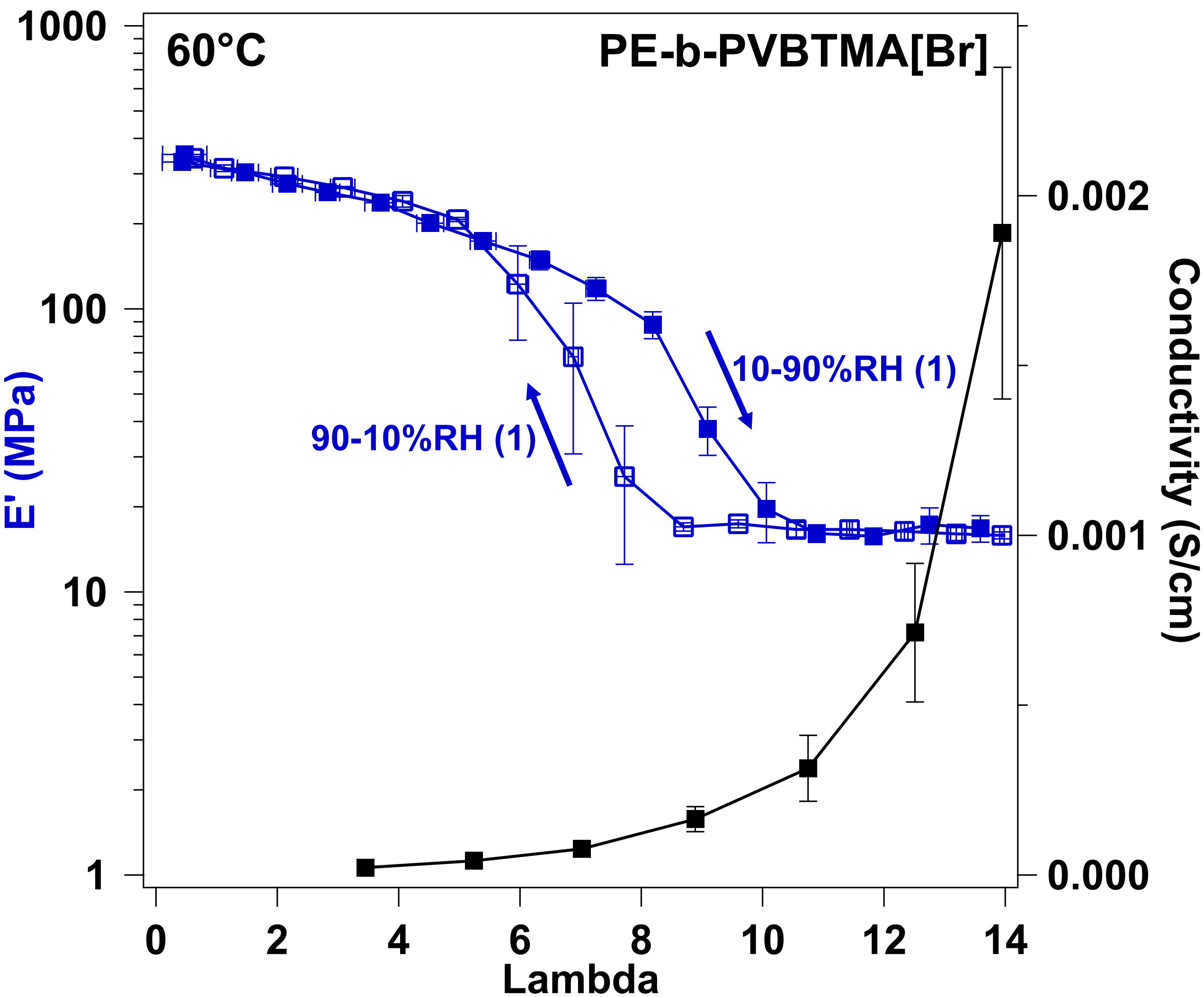
Hysteresis in narrow lambda range



Normalizing by lambda narrows hysteresis window

But hysteresis in transition remains

Conductivity increases after softening



Conductivity increases above λ~9, suggesting mechanical softening correlates with ion conduction

Conclusions

Mechanical properties are directly related to chemistry, IEC, and water sorption

Cationic functionalities increase stiffness, but plasticization due by water can severely soften and weaken membranes

Chain flexibility due to hygromechanical softening may enhance ion conduction

Membrane Publications

M.A. Vandiver, B.R. Caire, T.P. Pandey, Y. Li, S. Seifert, A. Kusoglu, D.M. Knauss, A.M. Herring, M.W. Liberatore. "Effect of hydration on the mechanical properties and ion conduction in a polyethylene-b-poly(vinylbenzyl trimethylammonium) anion exchange membrane", Journal of the Membrane Science, 497 (**2016**): 67-76.

B.R. Caire, M.A. Vandiver, M.W. Liberatore. "Mechanical testing of small, thin samples in a humidity controlled oven." *Rheologica Acta*, 15 (**2015**): 253-261

M.A. Vandiver, B.R. Caire, Z. Poskin, Y. Li, S. Seifert, D.M. Knauss, A.M. Herring, M.W. Liberatore. "Durability and performance of polystyrene-b-poly(vinylbenzyl trimethylammonium) diblock copolymer and equivalent blend anion exchange membranes." *Journal of Applied Polymer Science*, 132 (**2015**): 41596

M.A. Vandiver, B.R. Caire, J.R. Carver, K. Waldrop, M.R. Hibbs, J.R. Varcoe, A.M. Herring, and M.W. Liberatore. "Mechanical Characterization of Anion Exchange Membranes by Extensional Rheology under Controlled Hydration." *Journal of The Electrochemical Society*, 161 (**2014**): H677-H683

R. Janarthanan, J.L. Horan, B.R. Caire, Z.C. Ziegler, Y. Yang, X. Zuo, M.W. Liberatore, M. R. Hibbs and A. M. Herring. "Understanding anion transport in an aminated trimethylpolyphenylene with high anionic conductivity." *Journal of Polymer Science Part B:Polymer Physics*, 51 (**2013**): 1743-1750.

Y. Liu, J.L. Horan, G.J. Schlichting, B.R. Caire, M.W. Liberatore, S.J. Hamrock, G.M. Haugen, M.A. Yandrasits, S. Seifert, and A.M. Herring. "A Small-Angle X-ray Scattering Study of the Development of Morphology in Films Formed from the 3M Perfluorinated Sulfonic Acid Ionomer." *Macromolecules*, 45 (**2012**): 7495-7503.