Applications of Vacuum Insulation Panels in Extreme Environments

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NanoPore

What is NanoPore?

- 95 issued patents and >50 pending applications in porous materials since 1994.
- R&D, and production in Albuquerque, NM. UK development, marketing and distribution.
- Business segments:
  - Bulk nanoporous silica for advanced thermal insulation.
  - Nanoporous thin films (Nanoglass^{TM}) for low K dielectrics.
  - NanoCool^{TM} on-demand adsorption cooling.
  - High performance desiccants for energy storage
- NanoPore is the ***only*** producer of nanoporous carbon-silica vacuum insulation panels (VIP's)

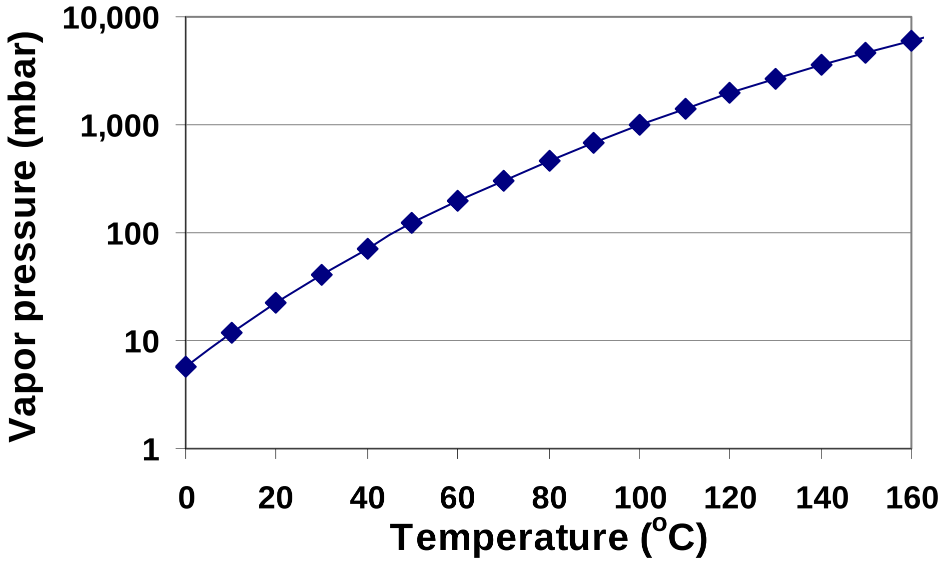
Nanoglass^{TM} is a registered trademark of Nanoglass LLC
NanoCool^{TM} is a registered trademark of NanoPore Incorporated

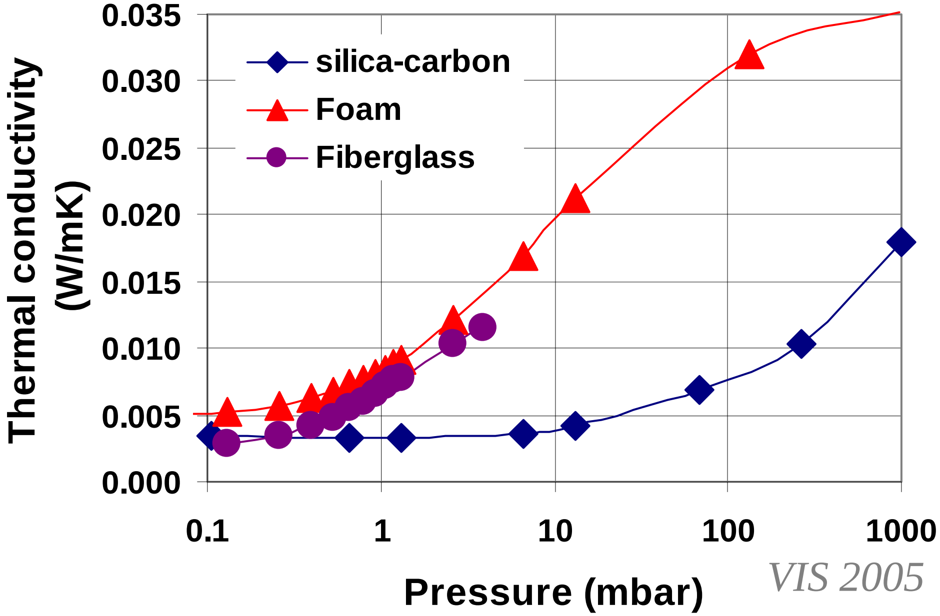
Expanding the VIP World

- VIPs three main commercial applications are domestic refrigeration, architectural, and controlled temperature packaging.
- However, there are other application where VIP's have greater value than for current markets such as:
  - Medium temperature (50-150 ^{o}C) for use in process, oil and condensate piping, consumer electronics, PEM fuel cells, and hot water heaters.
  - Cryogenic for LNG systems,
  - Flexible VIP's for apparel, flexible piping systems
  - Active VIP's for controlled temperature packaging and architectural use
- These applications are primarily limited by VIP lifetime

H_2O Vapor: **The** Problem at Higher Temperature!

- Water vapor pressure changes dramatically with temperature
- At normal VIP temperatures (<30 ºC), water vapor pressure is on the same order as the operating pressure for nanoporous silica-based VIP's so water is not a major problem
- The coldest side of the VIP sets the equilibrium vapor pressure
- For VIP's with micron pores (foams, fiberglass), H_2O is a major lifetime problem, even at sub-ambient temperatures

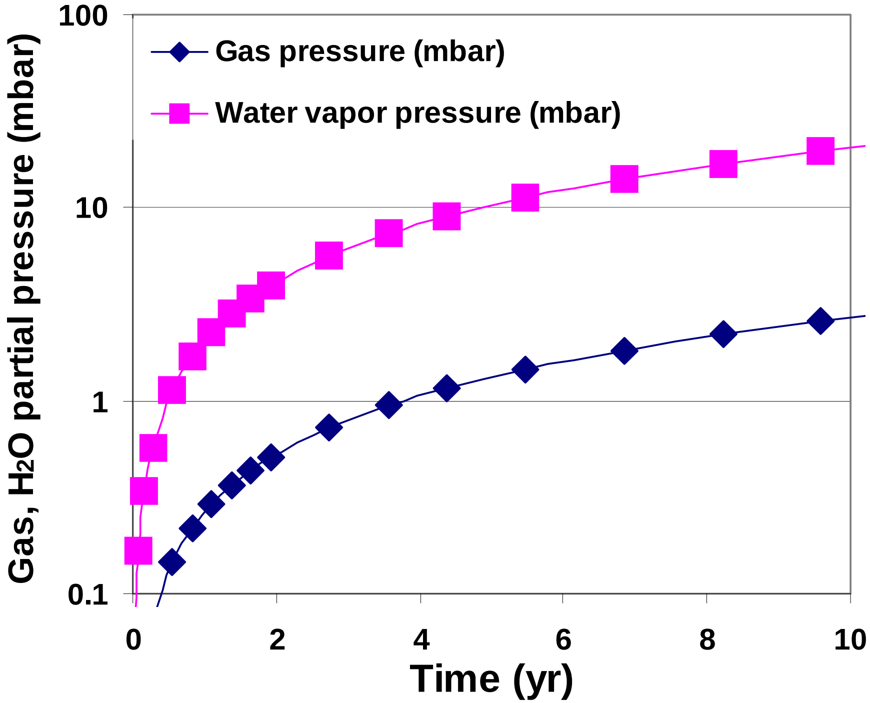




VIS 2005

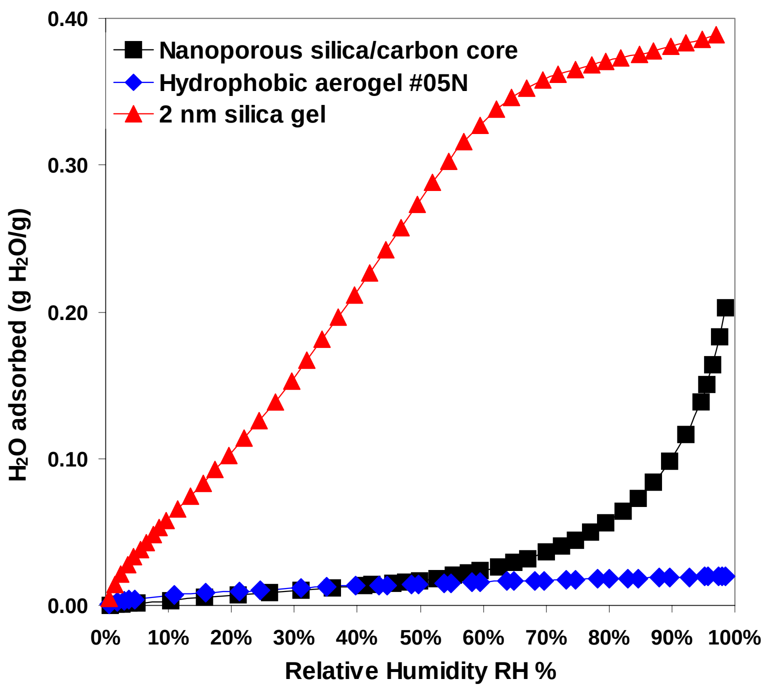
Water vapor permeation

- Increasing the VIP temperature from 0 to 40 ^oC yields an increase of >50x in water permeation rate
- Water and gas partial pressure modeling
  - 25 mm thick VIP
  - “Good” metalized barrier film
    - OTR =0.01 cm^3/m^2dbar
    - WVTR=0.02 g/m^2d
  - No seal permeation
  - Conditions; 40 ^oC and 100% RH
  - Water vapor dominates!

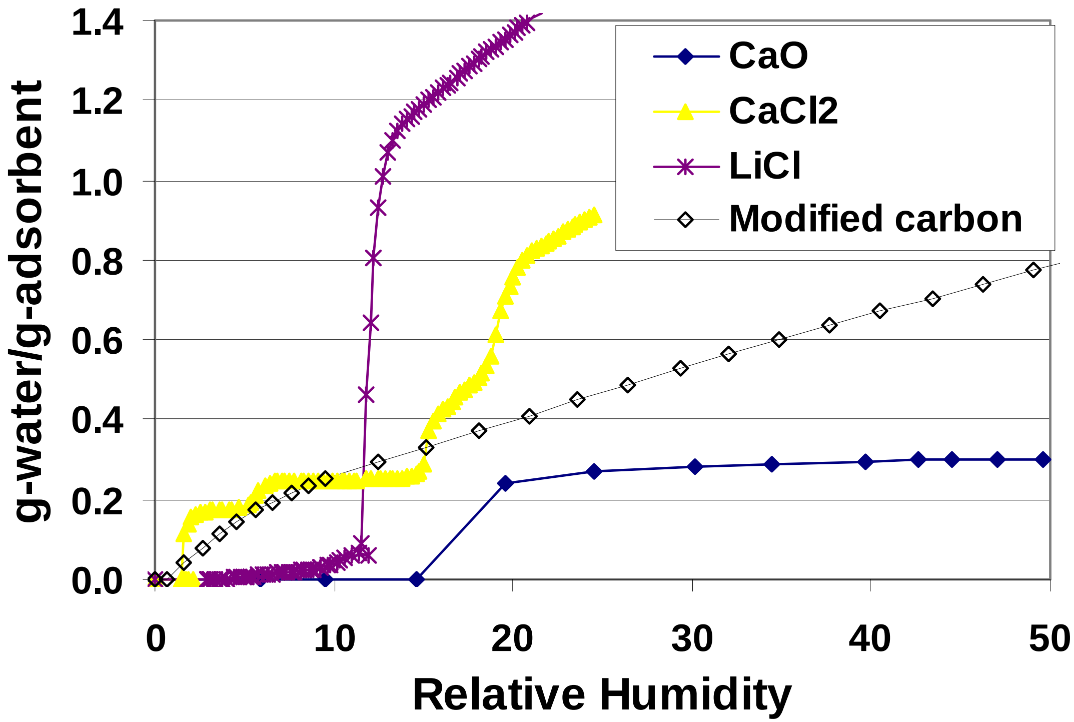


Water vapor adsorption

- Foams, fiberglass, and hydrophobic silica aerogels have minor water adsorption capability
- Nanoporous silica core material only starts to adsorb at 70% RH
- A typical 2 nm pore size silica desiccant adsorbs even at 10% RH
- If the VIP is at 50 °C
  - Water vapor pressure is ~100 mbar
  - For a silica VIP below 10 mbar, RH=10%
  - For fiberglass below ~0.1 mbar, RH=0.1%!
- If the VIP is at 100 °C
  - Water vapor pressure is ~1,000 mbar
  - For a silica VIP below 10 mbar, RH=1%
  - For fiberglass below ~0.1 mbar, RH=0.01%!
- For effective humidity below 10%, sorbents are the best approach



Water vapor chemisorption



- Hydration of oxides and salts such as CaO, $CaCl_2$, $MgCl_2$, LiCl
- Kinetics are much slower
- Particle size and pre-use drying conditions are very important
- Modified carbons (US patent #6,559,096) can be used to improve kinetics and avoid the need for handling fine particles.
- For low residual water partial pressure, the best adsorbents will provide ~0.2 grams of water per gram of adsorbent

How much water permeates (i.e., how much adsorbent)?

Temp	RH	g-H_2O	g-adsorbent
0	100	5	24
20	100	36	180
40	80	120	599
60	50	266	1,329
80	20	590	2,949
100	10	2,920	14,600

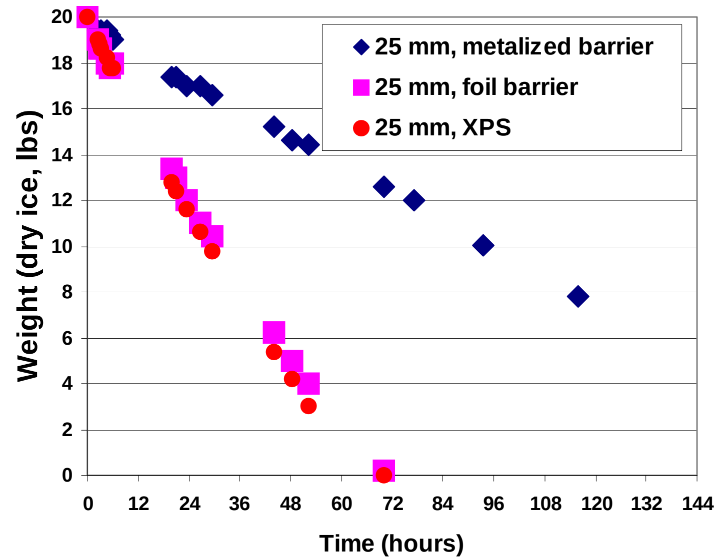
- Assume a typical film (WVTR=0.05g/m^{2}d)
- Assume a 1 m^2 VIP that it is 25 mm thick
- Amount of water depends upon temperature and RH
- For high temp., RH is normally low
- For a 10 year lifetime
- The VIP core weight is 2,000-6,000 grams
- To keep the RH low for long periods, the required desiccant can be greater than the VIP core weight and hence, impact thermal conductivity.
- Assumes both sides are at the same temperature. Permeation rate is dominated by the hot side and adsorption by the cold. One should always place the adsorbent on the cold side of the VIP.
- Assumes keeping the VIP residual pressure very low and is directly relevant for foam and fiberglass cores. For silica, because it has adsorbent capabilities and can operate at higher residual water vapor pressure, desiccants are only required for long-life applications above ambient temperature

Ultra-Barriers

- Two approaches to enhance VIP lifetime:
  - Add getters and desiccants to trap permeating gases and vapors (adds cost and environmental/safety problems)
  - Use barriers with better permeation resistance (Ultra-barriers)
- Two approaches to Ultra-barriers
  - Metal foil based
  - OLED approaches
- Measurement of OTR/WVTR when barriers are much better than the limits of standard permeation measurement instruments?
- One approach: Use Ca and measure the reaction of Ca to CaO and/or $Ca(OH)_2$. Measure the change gravimetrically or optically.

Metal Foil Ultra-Barriers

- Aluminum foil-based:
  - available commercially
  - high thermal conductivity of aluminum W/mK as compared to >0.004 W/mK VIP) causes severe thermal edge effects
  - CO_2 sublimation from a 27 L box
    - 25 mm fiberglass VIP with metalized film
    - 25 mm fiberglass VIP with Al foil film
    - 25 mm thick extruded polystyrene (XPS)



  - The Al foil VIP produced using a commercial VIP film was no better than XPS!
- Stainless steel or Nickel foil:
  - used in the Aura VIP's and some NanoPore high T VIP's
  - lower thermal conductivity (8-20 W/mK) reduces thermal edge effects
  - expensive
  - difficult to work with (brittle)
  - difficult to seal

CVD OLED Ultra-Barriers

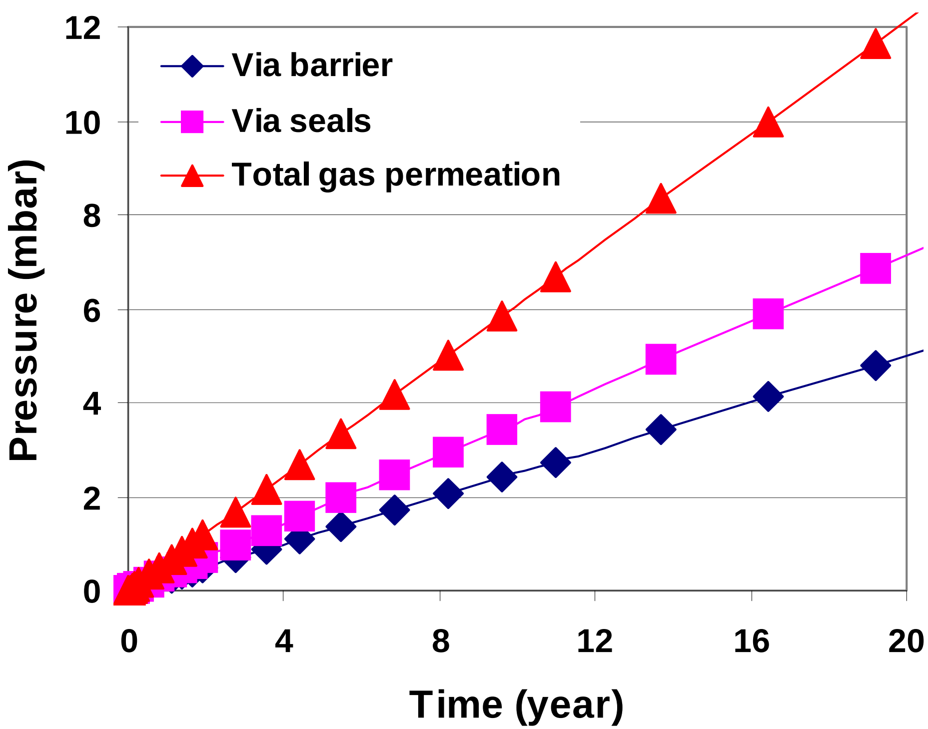
- OLED's have much more difficult OTR and WVTR requirements and there are exciting developments underway
- One approach uses multiple CVD-applied alternating polymer and ceramic (Al_2O_3) layers of 20-100 nm per layer.
- Advantages are:
  - More barrier layers can be applied than conventional VIP films
  - Thin polymer planarizes small-scale local roughness to minimize barrier layer defect density
  - Thin polymer layer increases permeation resistance between defects. Thickness is >100x thinner than conventional metalized barriers
  - Thermal conductivity essentially that of plastic (minimal edge effects)
- Permeation rates of $<5 \times 10^{-6}$ g/m^{2}day at 21 ^{o}C and 50% RH have been reported!
- Seal permeation remains a serious issue.

Seal Permeation

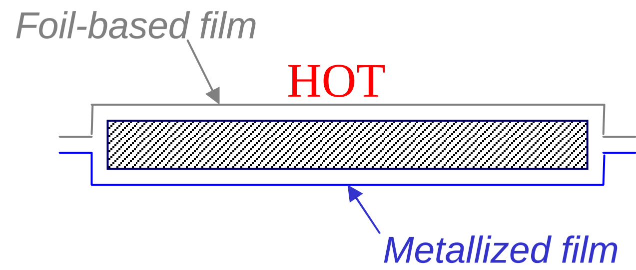
- No matter how good the barrier is in WVTR and OTR testing, we have to seal it!
- Polyolefin seal layers have WVTR ~50x greater than typical barriers but OTR can be up to 10^5x greater. But seal area is much smaller than the barrier area.

Modeling

- Assume:
  - 300 mm x 300 mm VIP
  - 25 mm thick
  - 50 micron seal layer thickness
  - 6 mm wide seals
  - OTR = 0.01 cm^3/m^2 d bar
  - VIP use at 40 ^oC and 50% RH
- Results:
  - H_2O vapor is not an issue for the seals
  - O_2/N_2 permeation through the seals is greater than through the barrier!
  - 20 year lifetime for silica panels is achievable
  - Foam and fiberglass VIPs need a O_2/N_2 getter for service life of even a few months if using heat seals.



VIP Design for Improved Barrier Performance

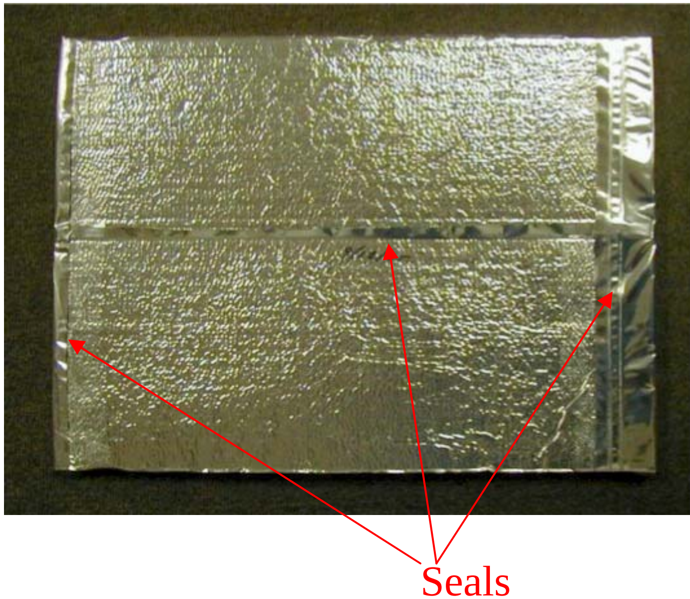


Panel Variables

- Asymmetric barrier film use
- Number and location of seals
  - “T” seal to remove 3rd seal from hot surface
  - Fold end seals over to cold side

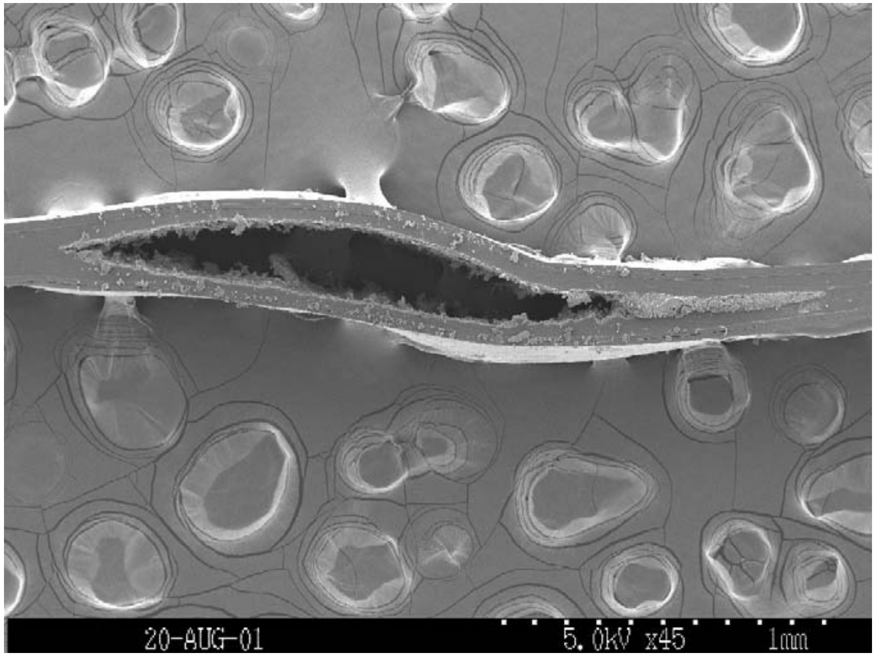
Barrier Variables

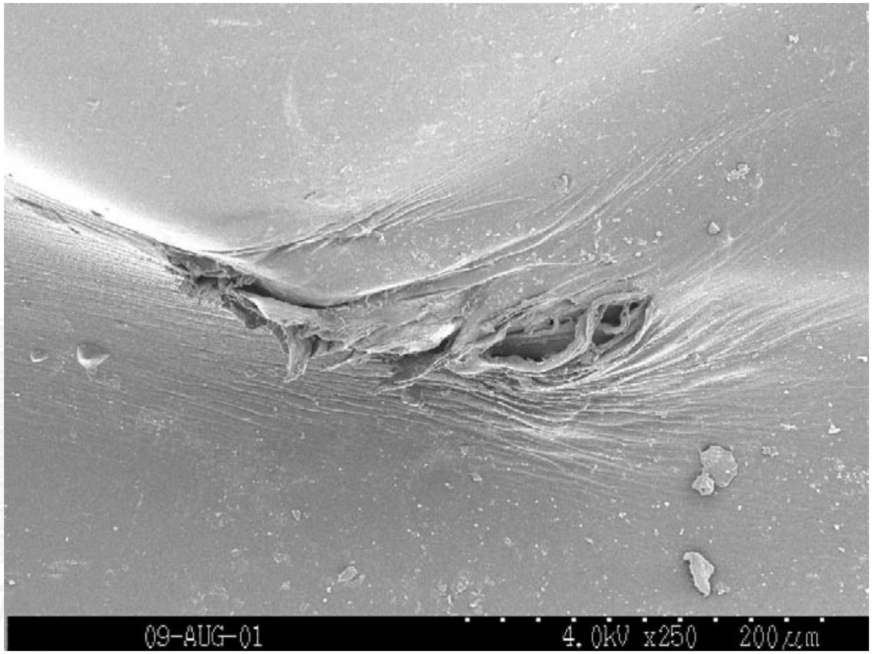
- Width of seal
  - 25mm typical in industry, >50mm difficult
  - Seal folding/edge binding
- Thickness of seal layer
  - Typical seal layer 50µm - robust
  - Thinner seal layers possible (5µm) but reliability suffers
- Seal material
  - PP & PE have good heat sealing properties
  - Alternate materials not readily available. PSAs?

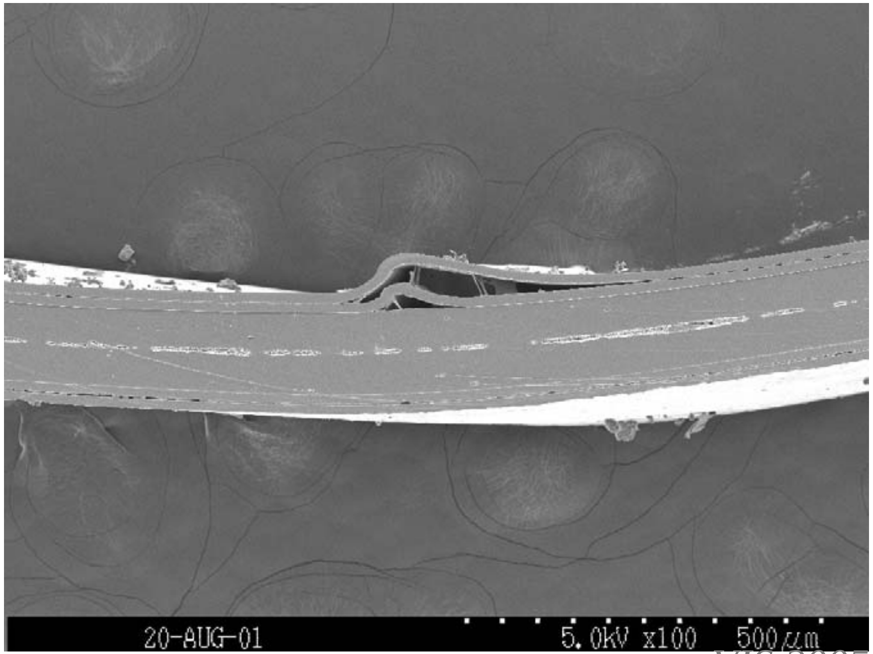


Thin Panel Flex Testing

- Thin (3mm) VIP subjected to repeated flex testing to failure (up to 400,000 cycles)
- Failure modes: seal failure, de-lamination, tearing
- System design that avoids or limits flexing of VIP in use is best prevention







Barrier Film Twisting

- We have previously noted reduced VIP lifetimes when barrier materials are flexed or creased.
- Controlled twisting on two different films. Films are rotated 440^{o} and moved 40 mm closer during each cycle.
- WVTR and OTR after 0, 2 and 10 cycles

Number of twists	WVTR 38 ^{o}C, 90%RH (g/m^2d)		OTR 23 ^{o}C, 75% RH, (cm^3/m^2dbar)	
	Barrier A	Barrier B	Barrier A	Barrier B
0	0.02	0.04	<0.01	0.02
2	0.12	0.09	1.50	1.89
10	0.25	0.17	4.29	5.67

- Small effect on water but >100x effect on oxygen!

Sample after 10 cycles

Keys to Long VIP Lifetime in Extreme Environments

- Employ a core material with pore sizes less than 100 nm rather than micron size to minimize gas and water vapor permeation effects
- Use high barrier materials but be aware of thermal edge effects
- For operating temperatures above 40 ^{o}C, consider the use of a desiccant even when using silica core material
- If there is a significant thermal gradient across the VIP, bring flaps & seals to the cold side whenever possible
- Minimize barrier film creasing/bending as much as possible during manufacture and in use