CERAMIC-MODIFIED SEPARATORS

Pushing the Limits of Cell Performance

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ENTEK

OUTLINE

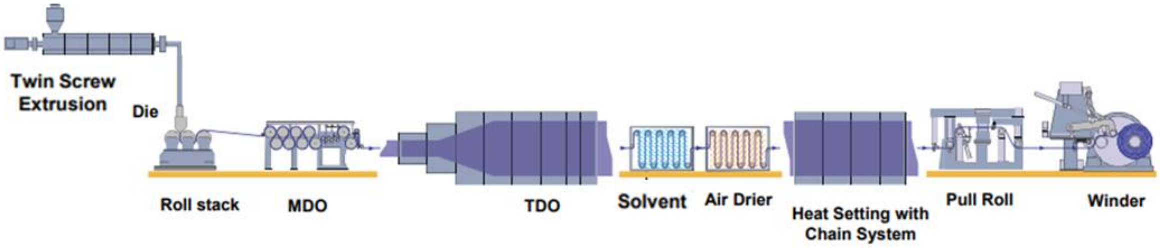
- ☐ Ceramic-Modified Separators
  - Surface Coatings
  - Bulk structure
  - Combination

- ☐ Surface Coatings
  - Base material
  - Particle size & type
  - Binder
  - Interfacial adhesion

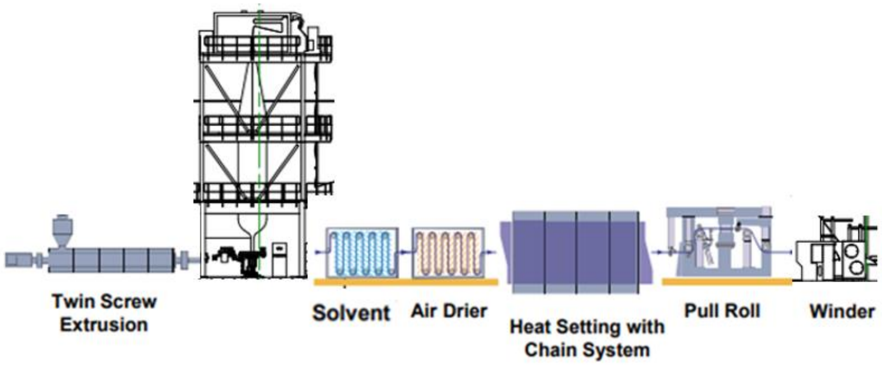
- ☐ Bulk incorporation
  - Loading level
  - Performance characteristics

LI-ION SEPARATOR PRODUCTION

- Dry Process
  - Isotactic PP
  - βeta → alpha crystal transformation
  - High MD orientation
  - PP monolayer or PP/PE/PP trilayer
  - 12-40 um thickness



- Wet Process
  - PE / oil phase separation
  - Biaxial orientation
  - Solvent extraction
  - 5-25 um thickness



CERAMIC COATING APPROACH

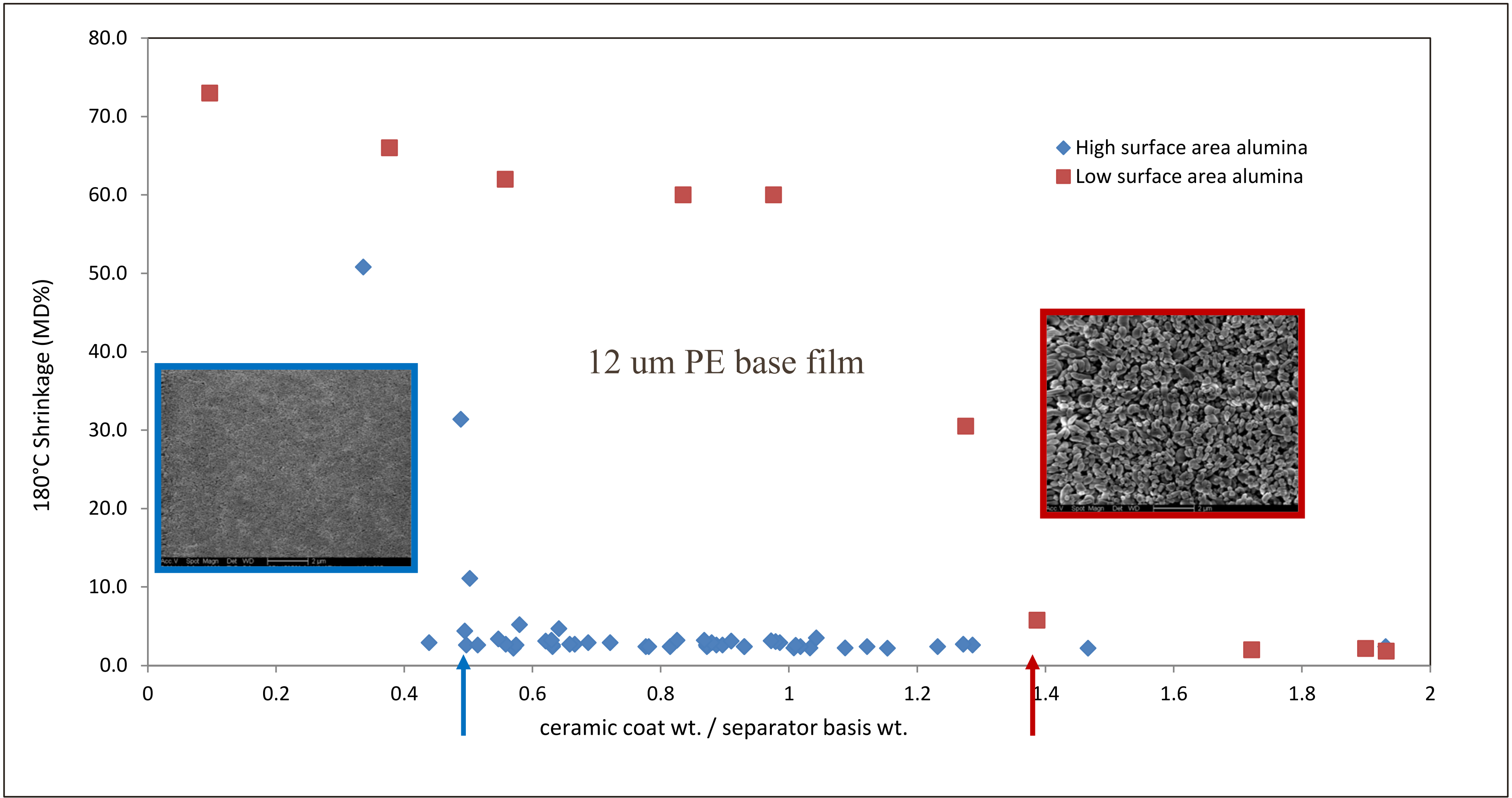
- ☐ Water-based dispersions
  - Dip coating process
  - Double side coating
  - Meyer rods control coat wt.

- ☐ Inorganic ***nanoparticles***
  - Alumina
  - Boehmite
  - Other

- ☐ Ultralow binder contents
  - Oligomers
  - Polymers
  - Small molecules

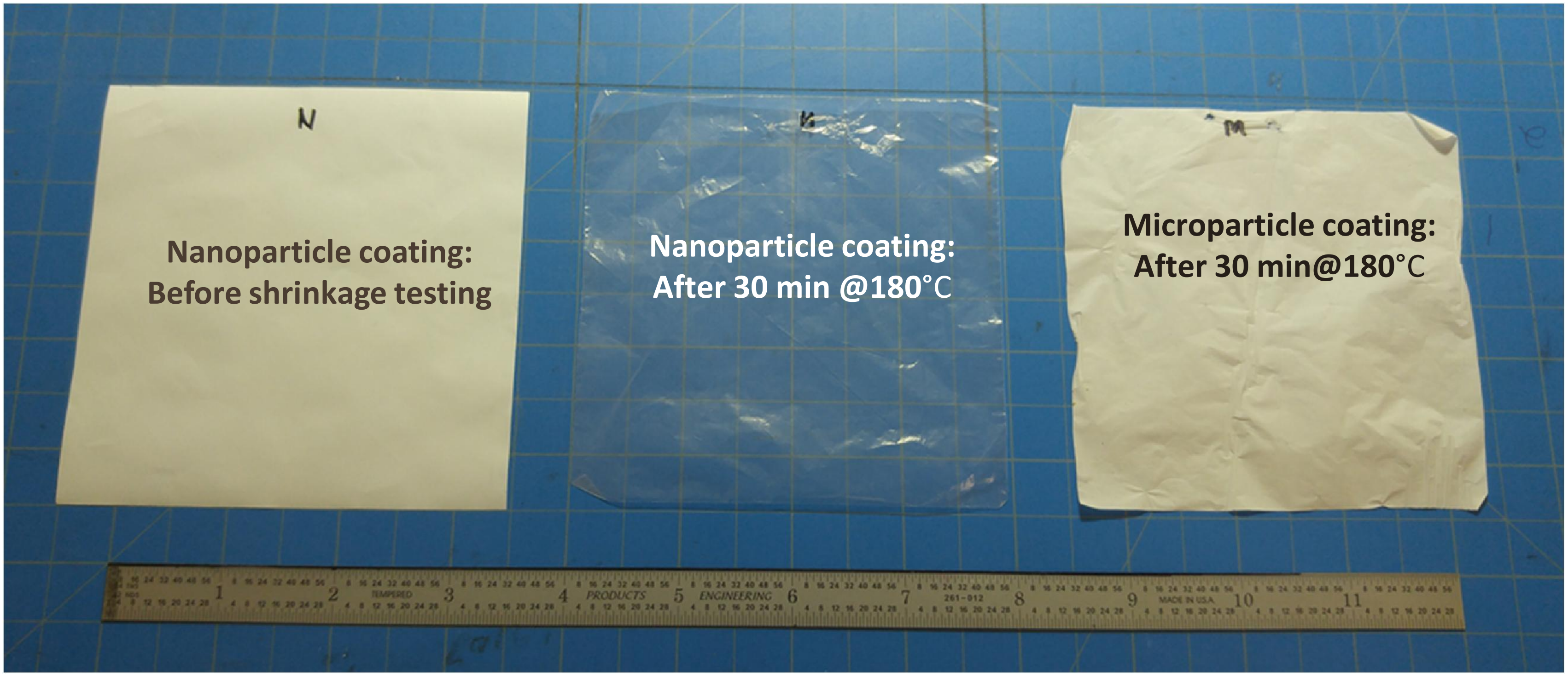
R&D Coater

PE BASE FILM --- PARTICLE SIZE & COAT WEIGHT



ENTEK separator with alumina nanoparticle coatings required 60% less ceramic to achieve excellent high temperature dimensional stability

THERMAL SHRINKAGE AT 180 C

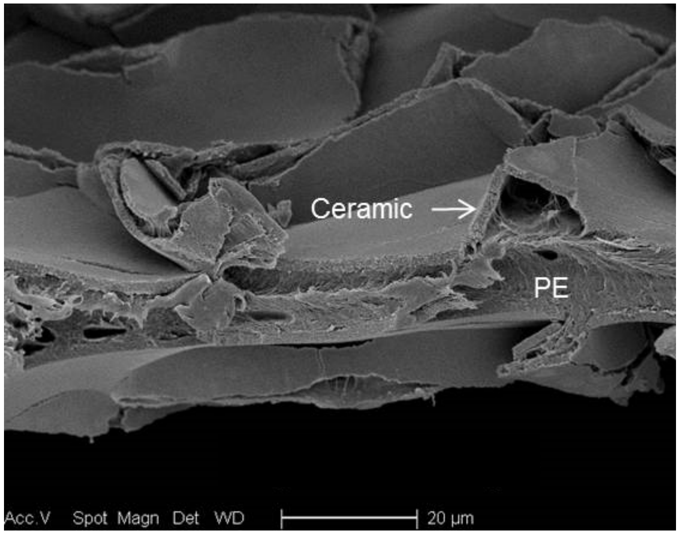

Nanoparticle coating: Before shrinkage testing

Nanoparticle coating: After 30 min @180°C

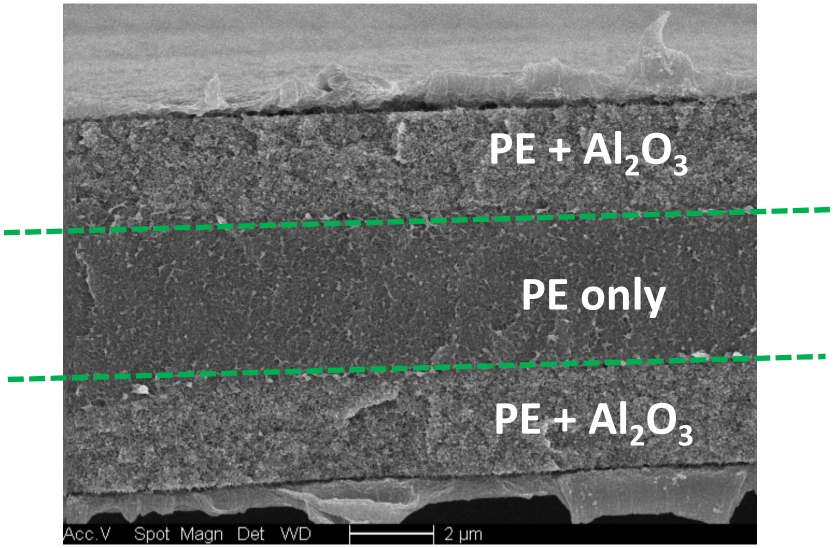
Microparticle coating: After 30 min@180°C

Note that the separator with the nanoparticle coating exhibits minimal light scattering and is transparent after the 180 C oven test

HTDS – HIGH TEMPERATURE DIMENSIONAL STABILITY



High shrinkage and buckling occur below critical ratio

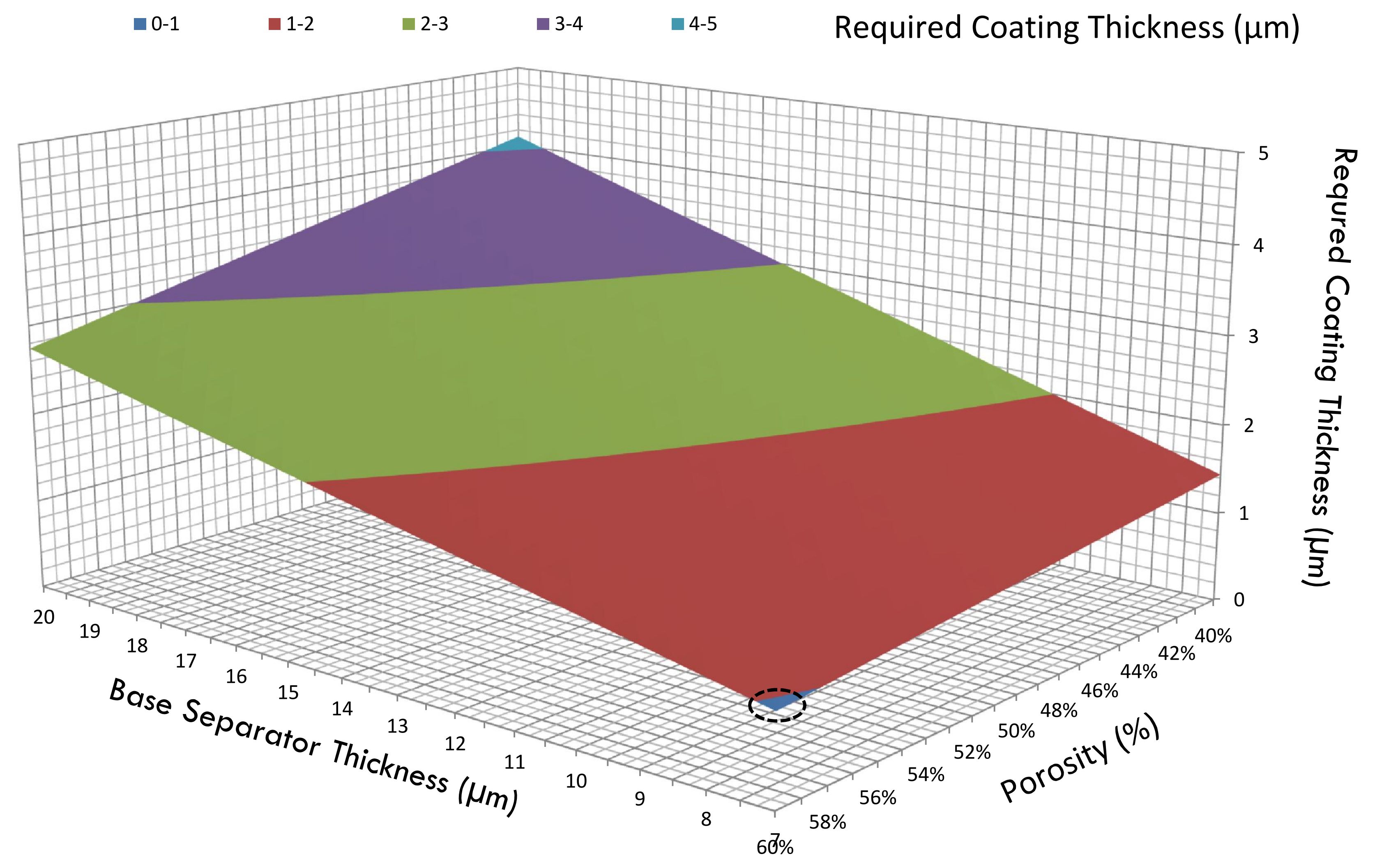


Low shrinkage and uniform shutdown occur above critical ratio

Same alumina nanoparticle dispersions were used for coating each example

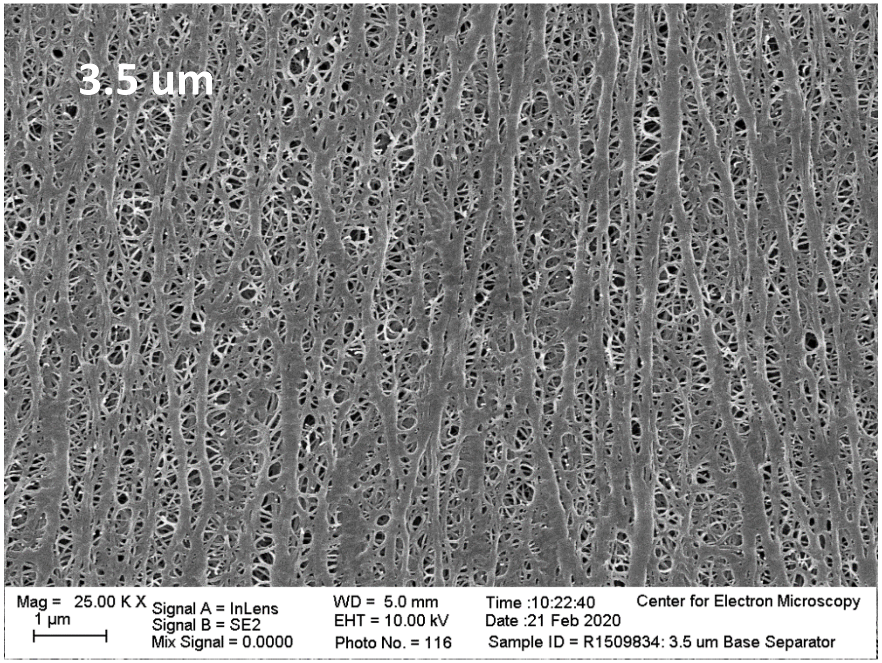
PUSHING THE DESIGN LIMITS

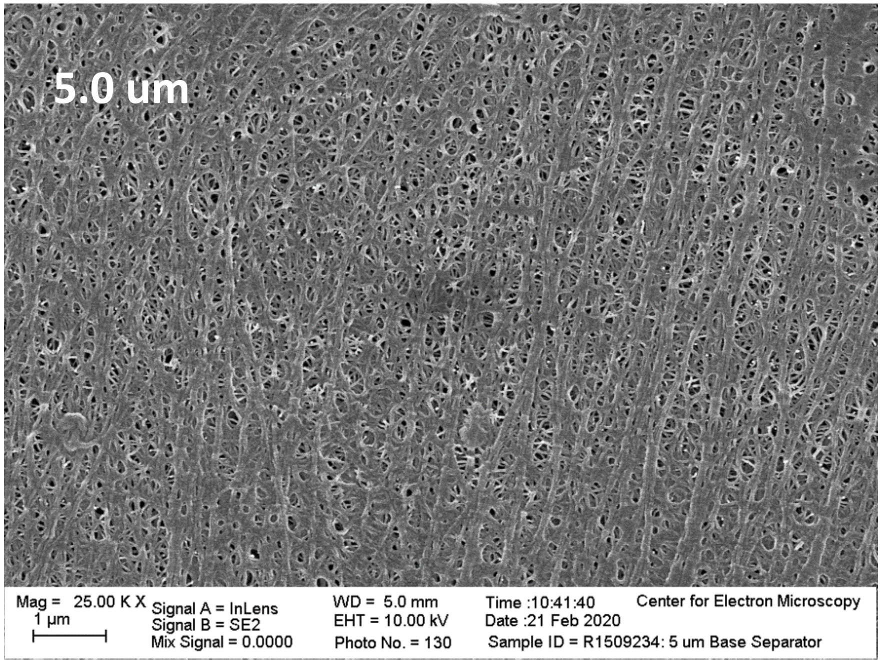
Alumina nanoparticles; Critical ratio = 0.5 ; Coating porosity = 60%



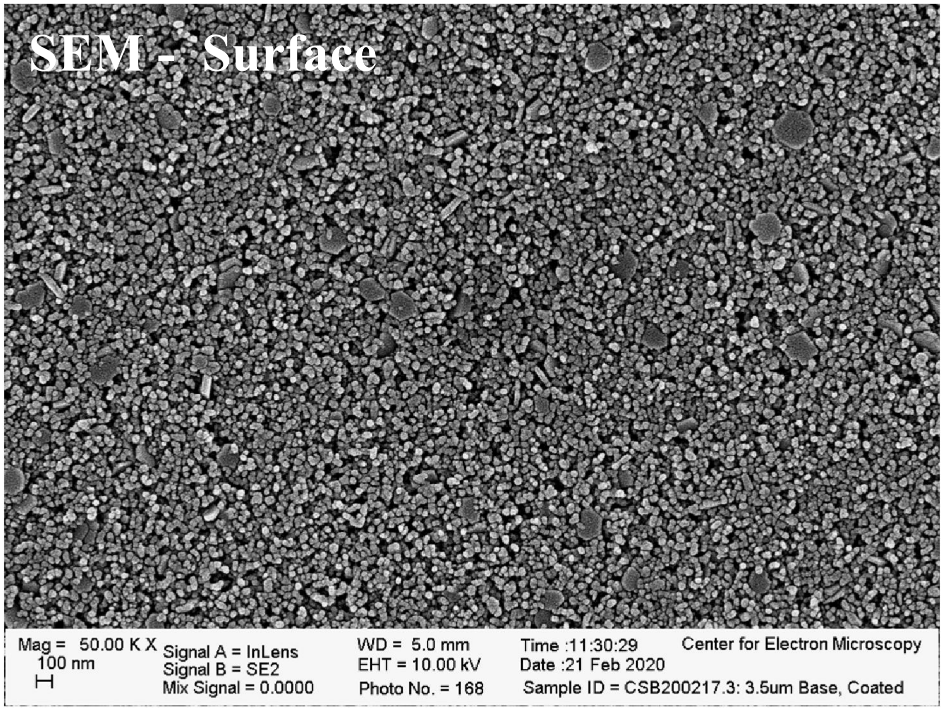
WHAT IF WE GO EXTREMELY THIN ?

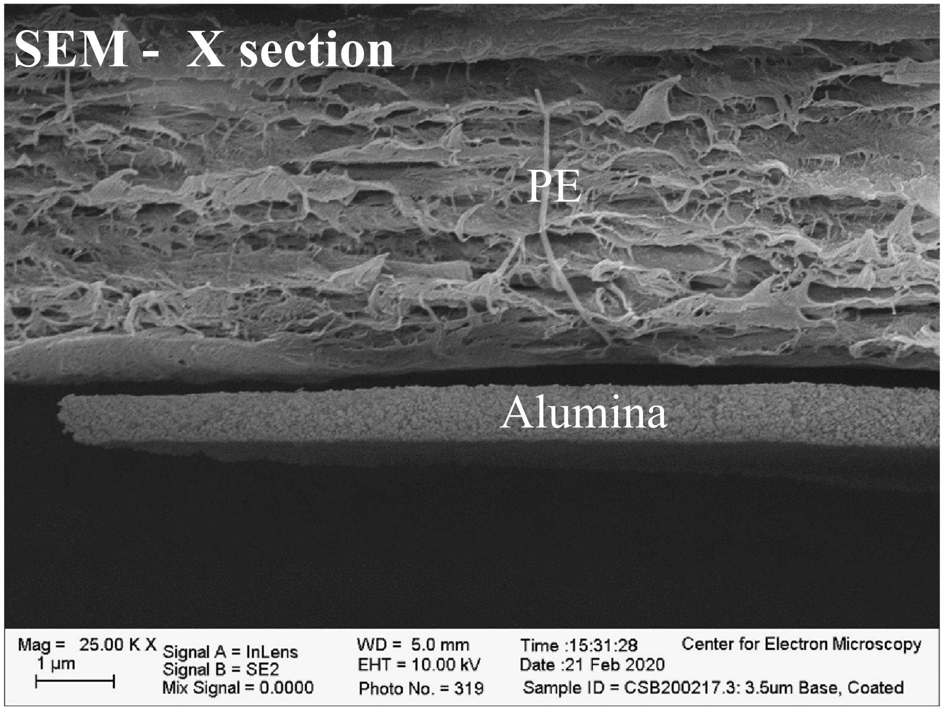
Base Separator	Porosity	Thickness Calculated	Basis weight	Gurley	Puncture	120°C shrinks 30 min MD	120°C shrinks 30 min TD	MD Tensile	TD Tensile	MD Elong%	TD Elong %
	%	µm	g/m2	s/100cc	gf	%	%	kg/cm2	kg/cm2	%	%
5µm Nominal Thickness	39	5.0	2.9	107.1	172.7	10.3	0.7	1345	1029	30	142
3.5µm Nominal Thickness	36	3.6	2.2	98.0	151.5	11.1	2.0	1772	1292	24	131





3.5 UM PE + ALUMINA NANOPARTICLES





High Temperature Dimensional Stability (< 5% shrinkage at 180 C)

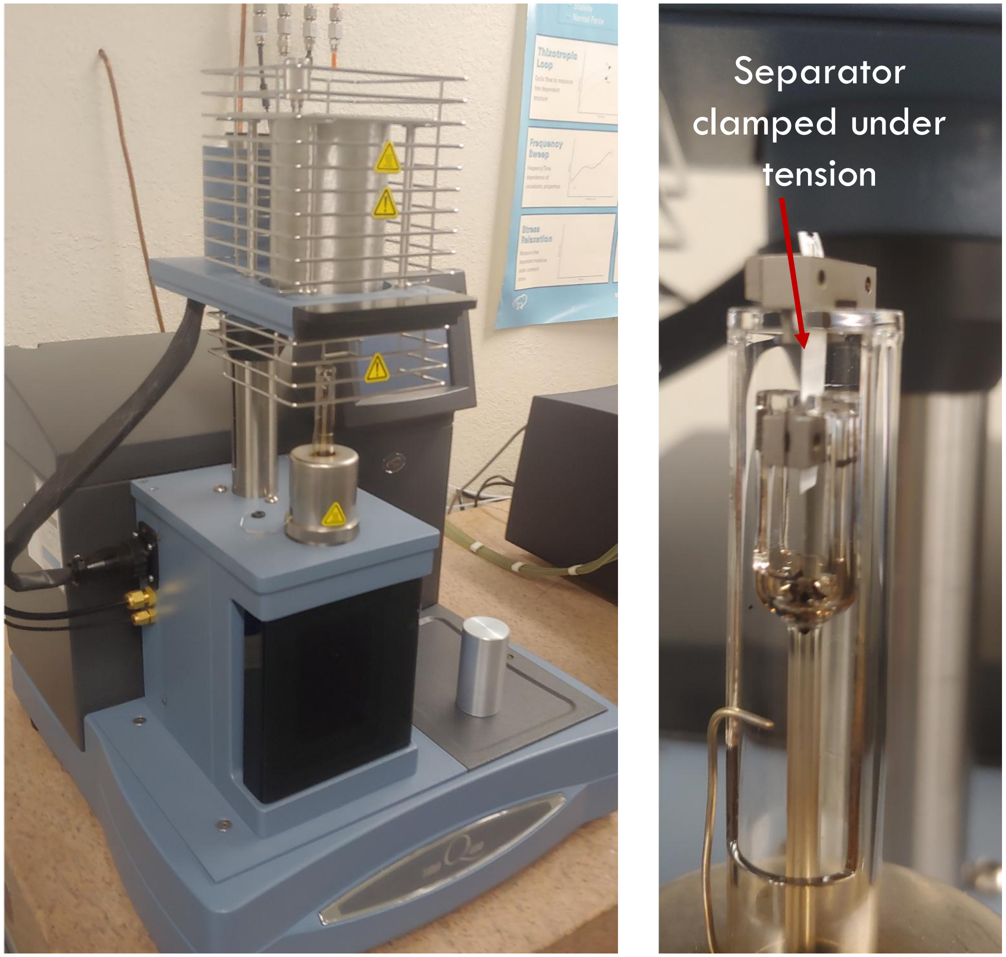
- critical ratio = 0.95 for 3.5 um base separator
- critical ratio = 0.75 for 5 um base separator

THERMOMECHANICAL ANALYSIS

- For TMA testing, separators were clamped under tension, and base separator displacement was measured as a function of temperature.

- Initial TMA conditions:
  - 0.005 -0.03N tension load
  - 10°C/minute ramp rate
  - 5mm width x 5.6 mm length
  - nitrogen

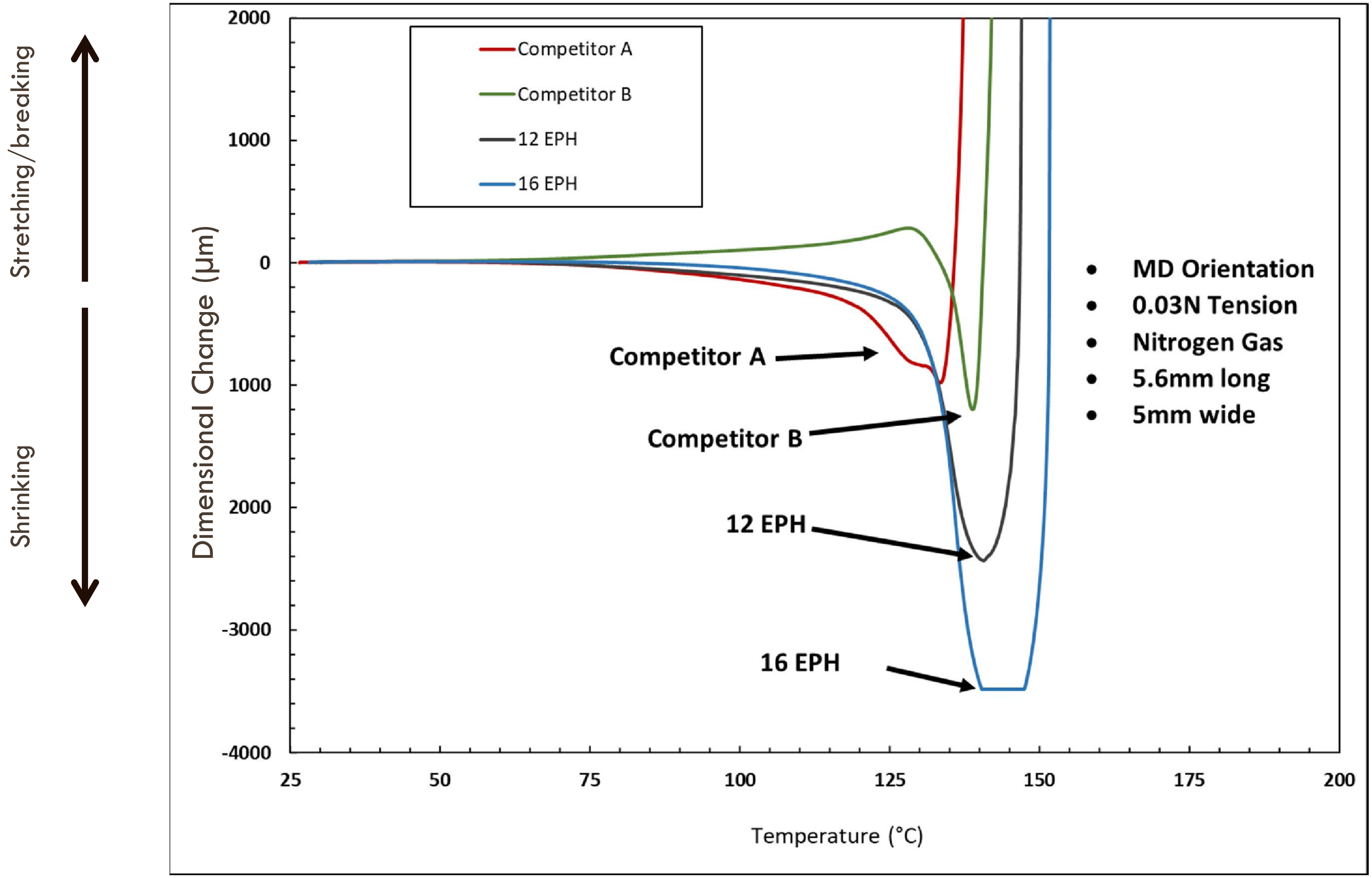
- TMA was performed on various separators in the machine and transverse direction.



Separator clamped under tension

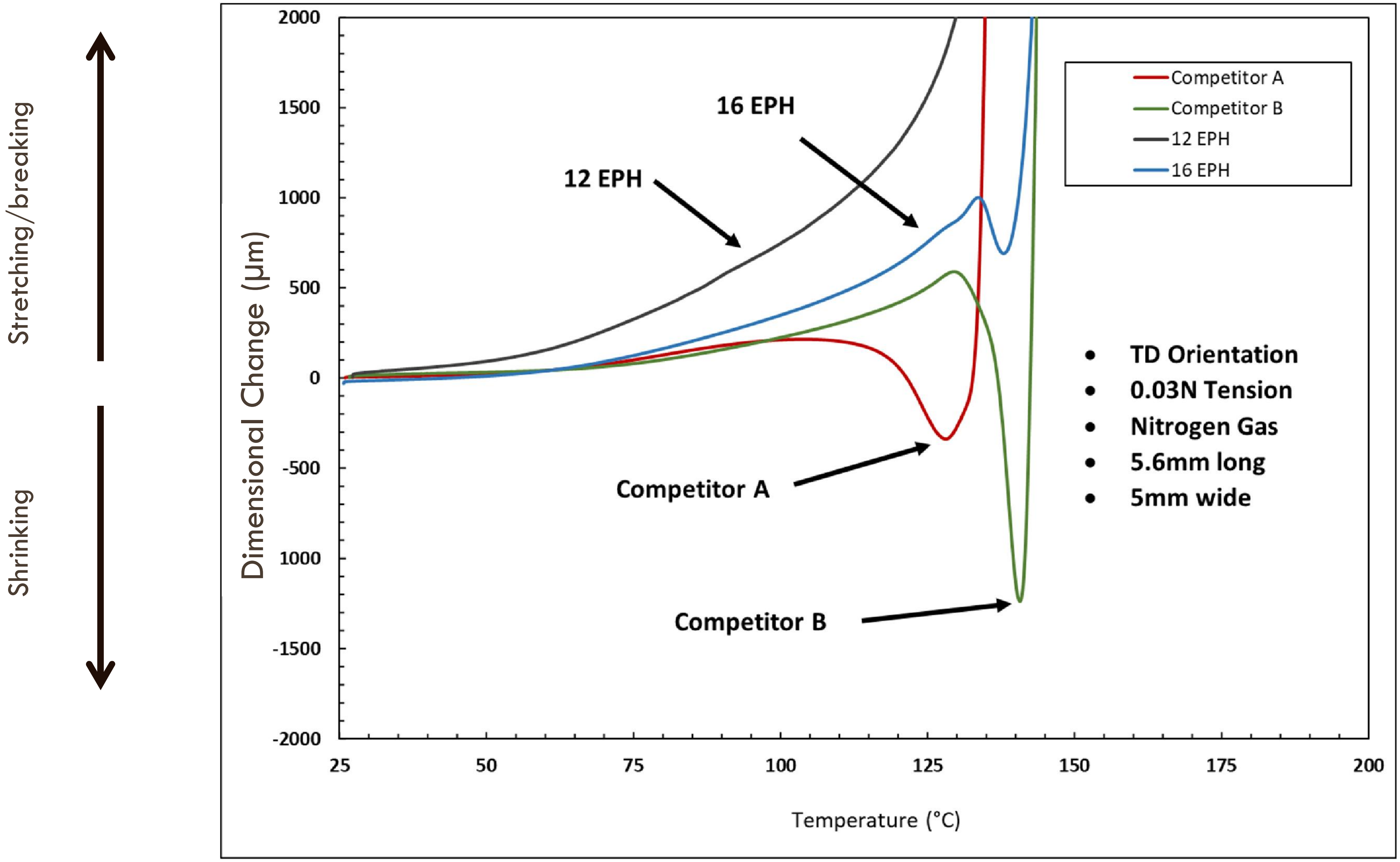
TMA Q400 (TA Instruments)

TMA: BASE SEPARATOR, MD ORIENTATION



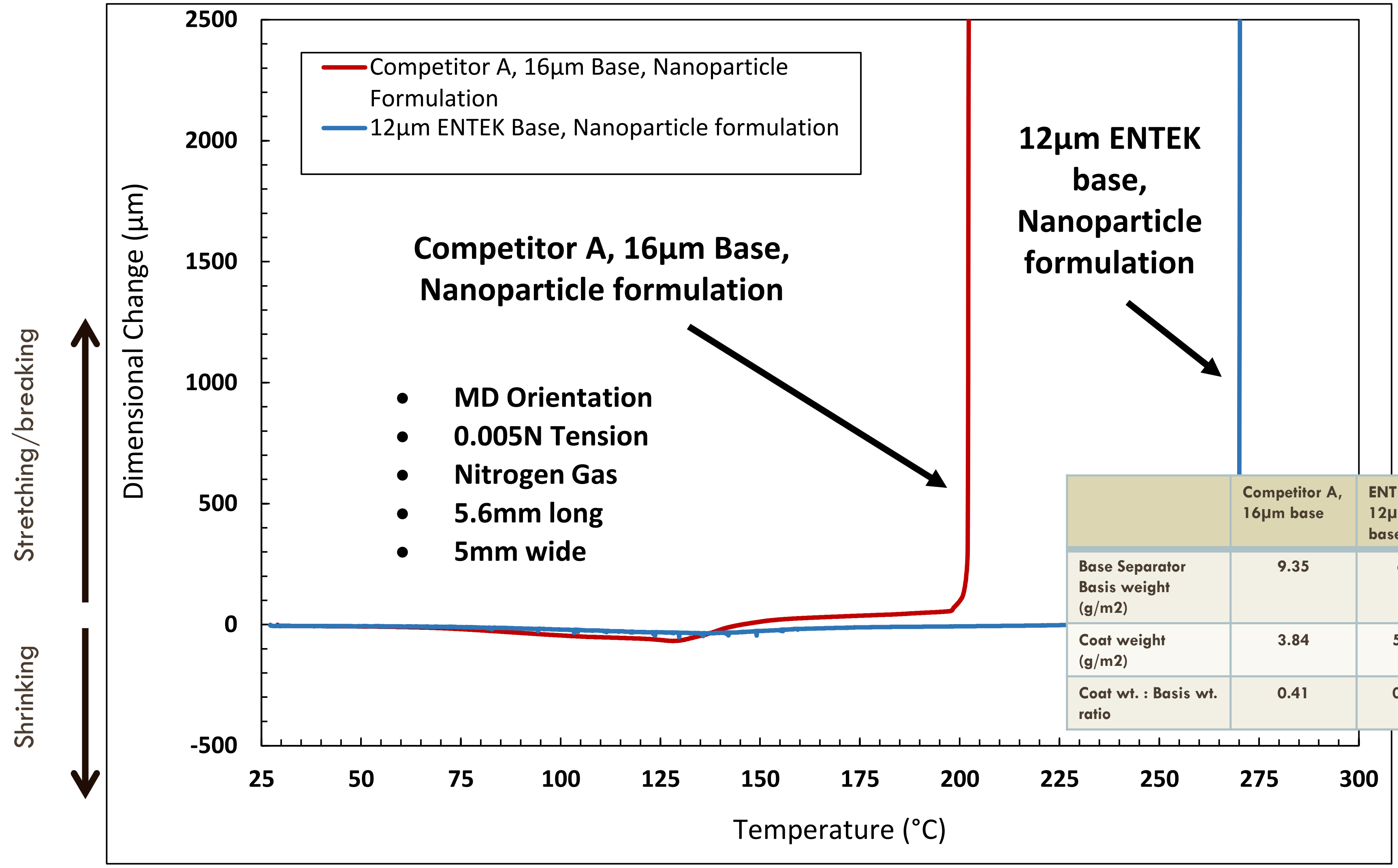
- **MD Orientation**
- **0.03N Tension**
- **Nitrogen Gas**
- **5.6mm long**
- **5mm wide**

TMA: BASE SEPARATOR, TD ORIENTATION



- TD Orientation
- 0.03N Tension
- Nitrogen Gas
- 5.6mm long
- 5mm wide

HOW DOES PE BASE FILM IMPACT COATING REQUIREMENTS ?



Competitor A, 16µm Base, Nanoparticle formulation

12µm ENTEK base, Nanoparticle formulation

- **MD Orientation**
- **0.005N Tension**
- **Nitrogen Gas**
- **5.6mm long**
- **5mm wide**

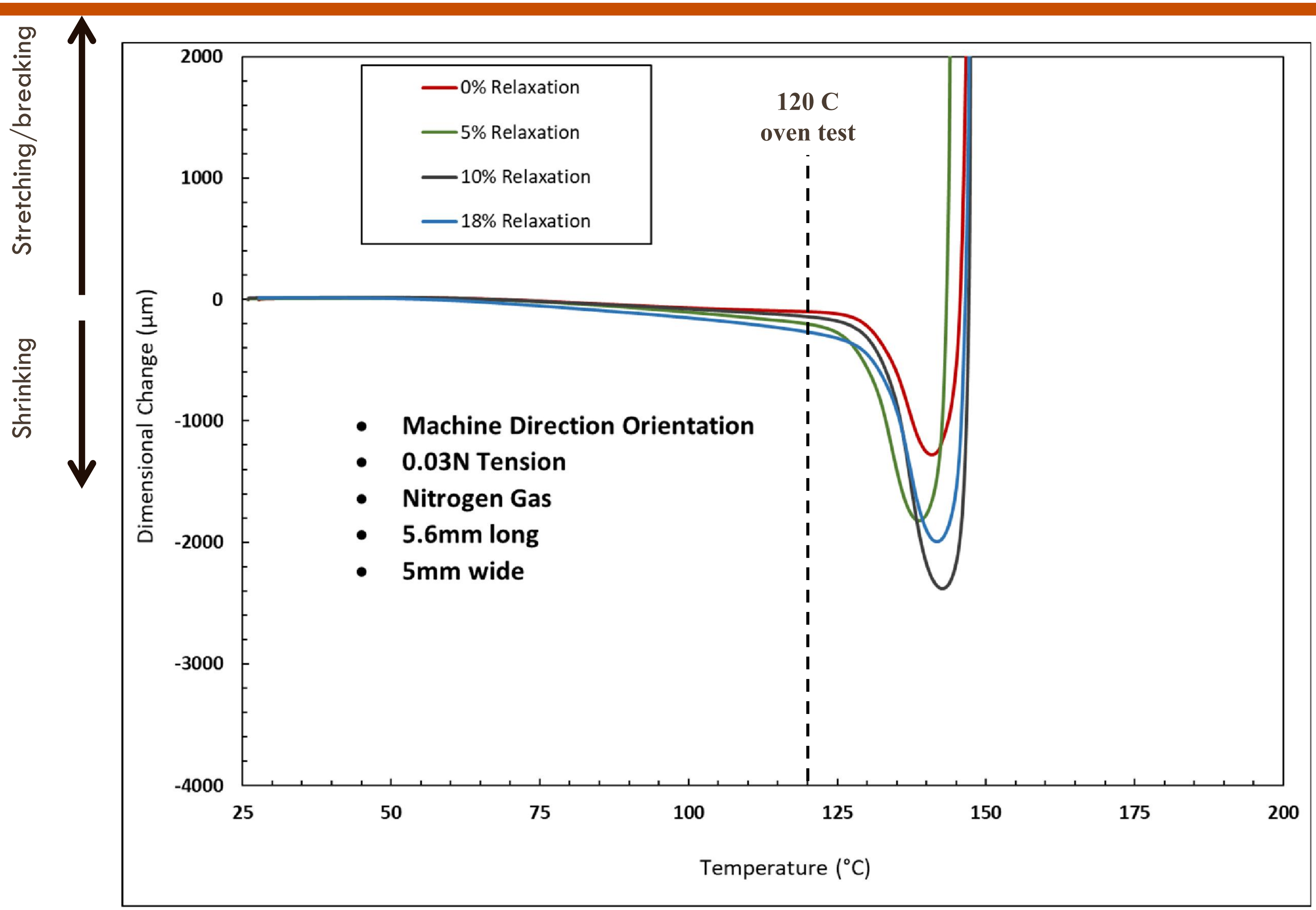
	Competitor A, 16µm base	ENTEK, 12µm base
Base Separator Basis weight (g/m2)	9.35	6.4
Coat weight (g/m2)	3.84	5.37
Coat wt. : Basis wt. ratio	0.41	0.84

WHAT ARE IMPLICATIONS OF SEPARATOR PROCESS CONDITIONS ON HTDS COATING REQUIREMENTS ?

- Same formulation, temperatures, and process conditions except for % relax during heat stabilization
  - 18% relax
  - 10% relax
  - 5% relax
  - 0% relax

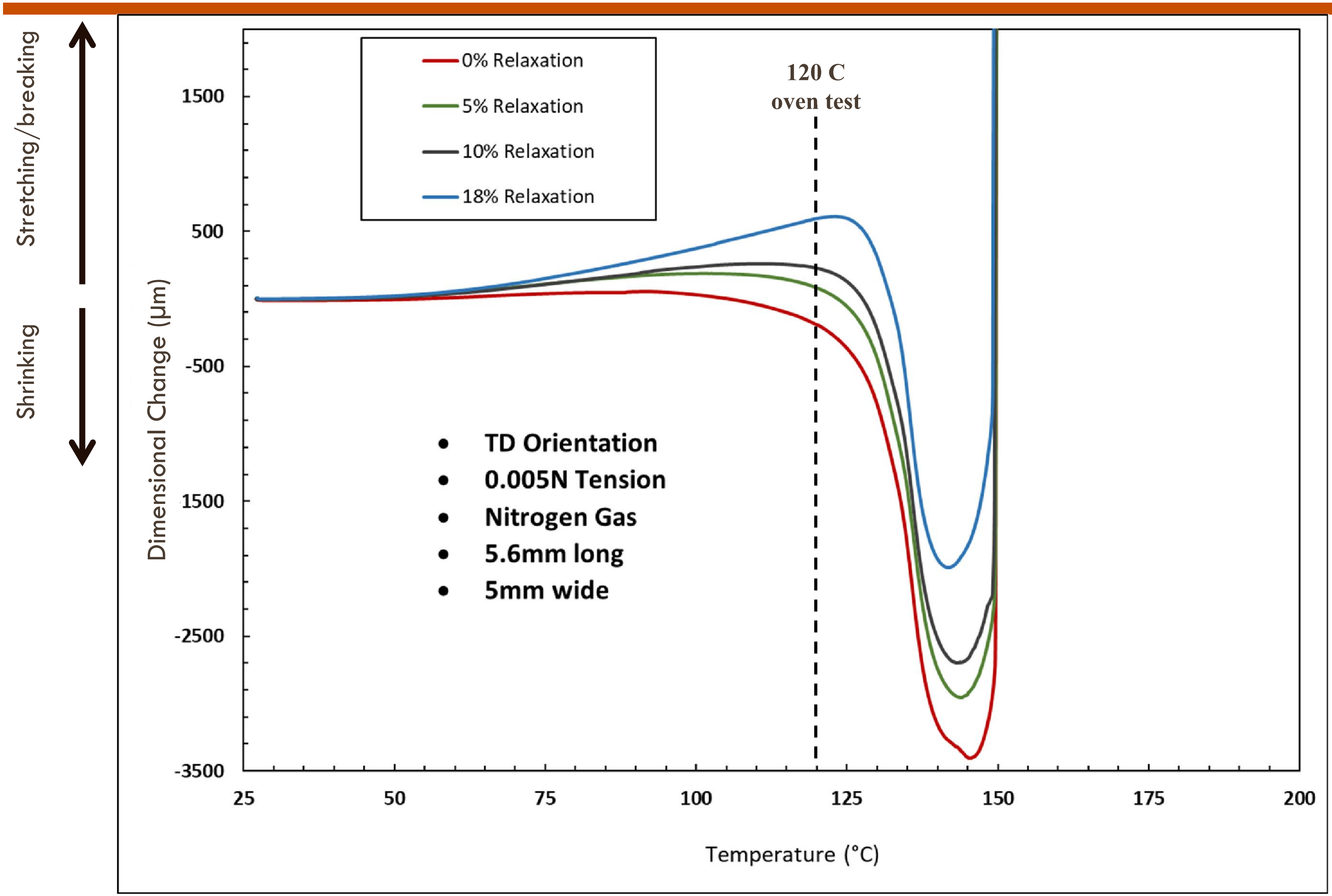
						Thermal Shrinkage 30 min @ 120 C	
Roll Number	Relax	Basis Weight (g/m2)	Porosity (%)	Avg. Thickness (um)	Gurley (s/100 cc)	MD	TD
S1509I31	Control 18%	5.62	52.6	12.4	62	9.1	5.3
S1509J31	10%	5.20	55.7	12.4	55	9.1	10.1
S1509K31	5%	4.90	56.9	11.8	49	9.1	13.7
S1509L31	0%	4.68	57.9	12.0	47	9.0	17.4

HOW DOES TDO RELAXATION IMPACT TMA - MD RESPONSE?



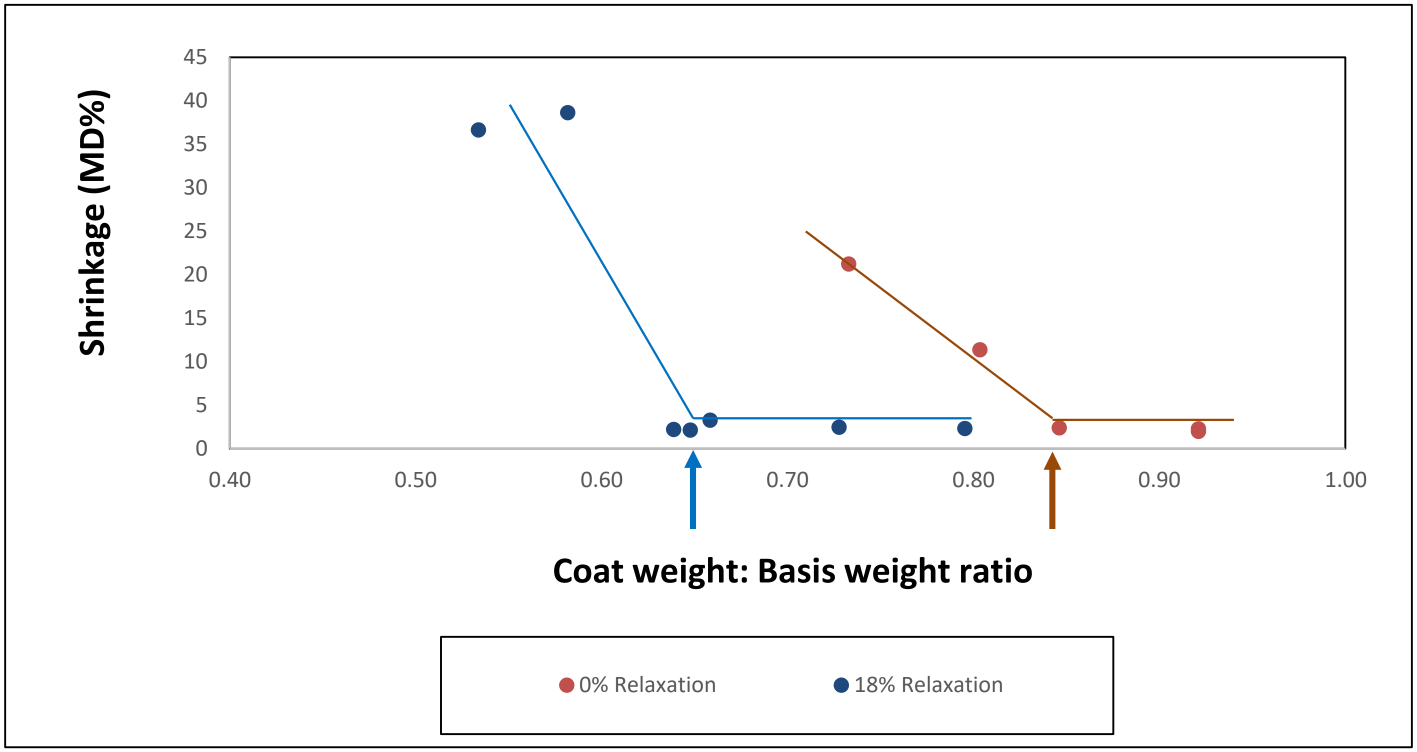
- Machine Direction Orientation
- 0.03N Tension
- Nitrogen Gas
- 5.6mm long
- 5mm wide

HOW DOES TDO RELAXATION IMPACT TMA - TD RESPONSE?



- **TD Orientation**
- **0.005N Tension**
- **Nitrogen Gas**
- **5.6mm long**
- **5mm wide**

CRITICAL COAT WEIGHT VS TDO RELAXATION



- Alumina nanoparticle coating formulation with 3% polymer binder
- Dip coating process with Meyer rods to control coat weight
- Shrinkage test : 30 min at 180 C

QUICK SNAPSHOT

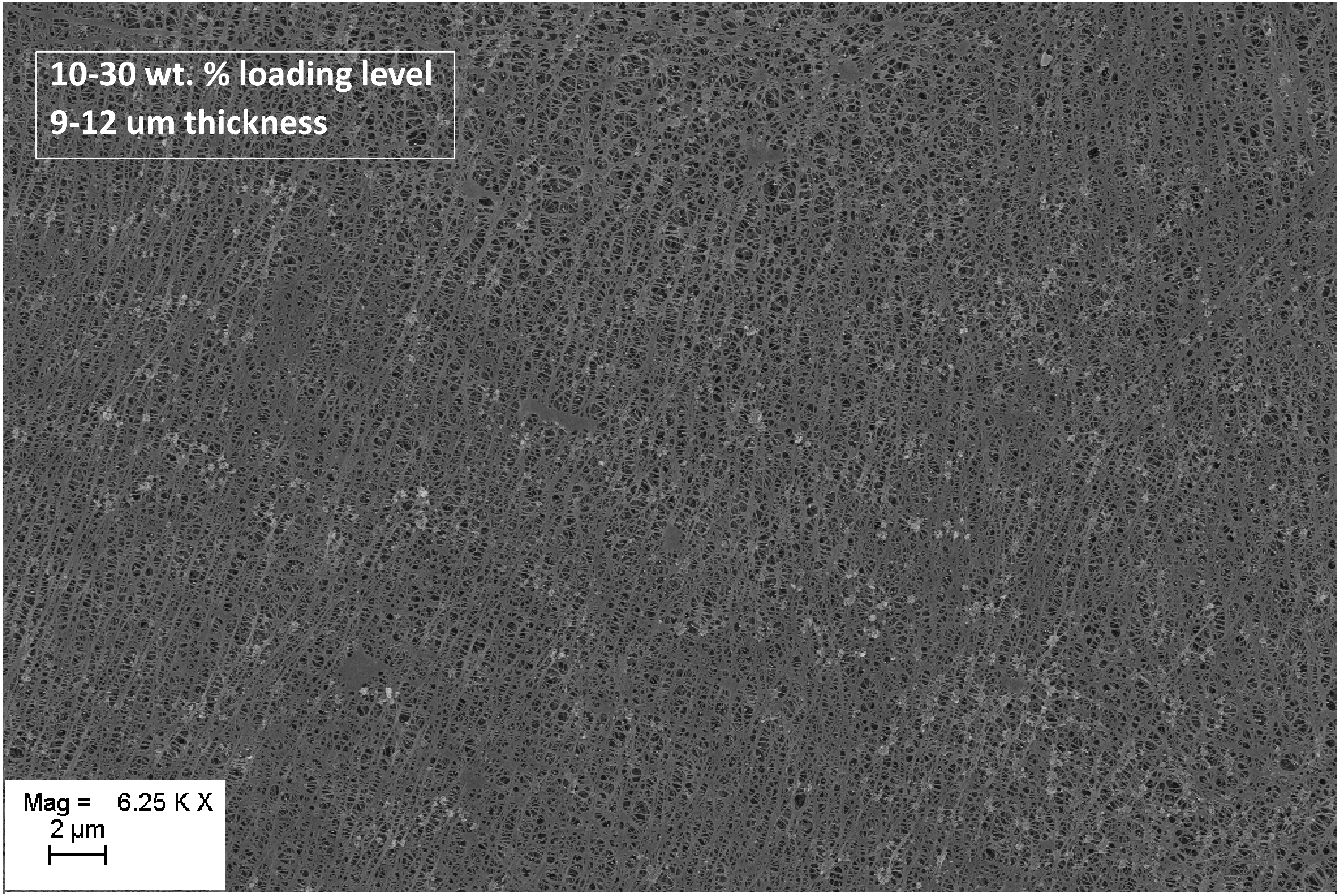
- Separators have become a complex and even more critical part of Li-ion battery design
  - Ceramic coatings are necessary to prevent oxidation from high voltage cathodes
  - High temperature dimensional stability both above and below PE melting point is important
  - In separator designs for electrode adhesion, the PE/ceramic interface is often the weak point

- Not all PE base separators are created equal
  - Process conditions impact coating requirements
  - UHMWPE content delivers higher melt down temperature

- Not all ceramics are created equal
  - Nanoparticles enable lower coat weights and overall thickness

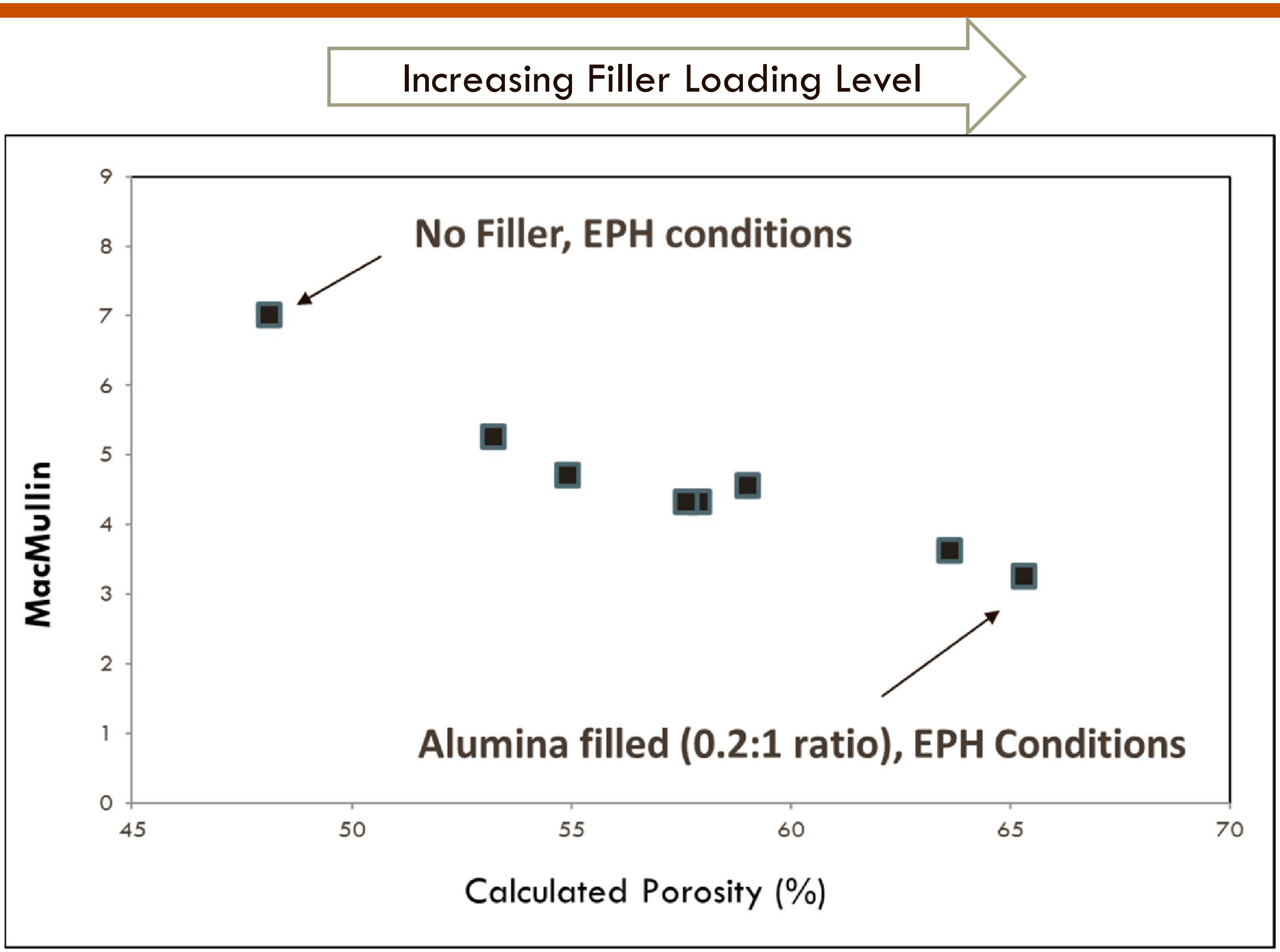
- From a cost standpoint, it is better to change PE thickness and porosity, rather than add more ceramic as part of the coating layer(s)

CERAMIC-FILLED SEPARATORS


10-30 wt. % loading level

9-12 um thickness

ALUMINA-FILLED SEPARATOR FOR HIGH POWER

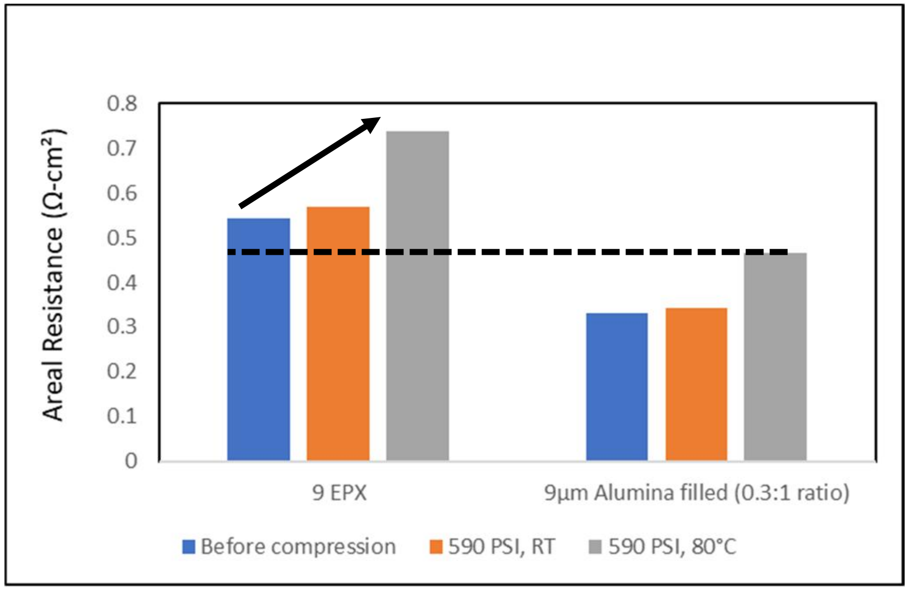


Porosity and ionic conductivity increased (decrease in MacMullin number) with increasing filler loading level.

ENTEK

COMPRESSION VS IONIC RESISTANCE

Sample	ID #	Condition	Average Gurley (s/100cc)	EMVECO Thickness (µm)	Areal Resistance (Ω-cm^2)	Macmullin (Normalized by original EMVECO thickness)
9 EPX	Q150T434	No compression	54.0	9.4	0.543	4.5
9 EPX	Q150T434	590 PSI, RT	61.7	8.9	0.568	4.7
9 EPX	Q150T434	590 PSI, 80°C	96.0	8.3	0.739	6.1
9µm, Alumina filled (0.3:1)	Q150DM31	No compression	28.0	10.0	0.332	2.8
9µm, Alumina filled (0.3:1)	Q150DM31	590 PSI, RT	32.0	8.9	0.343	2.9
9µm, Alumina filled (0.3:1)	Q150DM31	590 PSI, 80°C	48.7	8.4	0.466	4.0

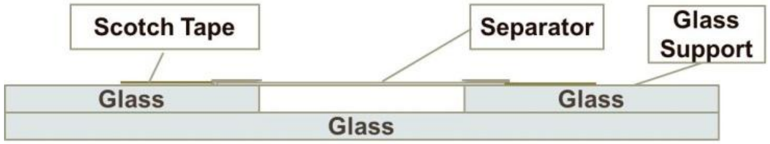


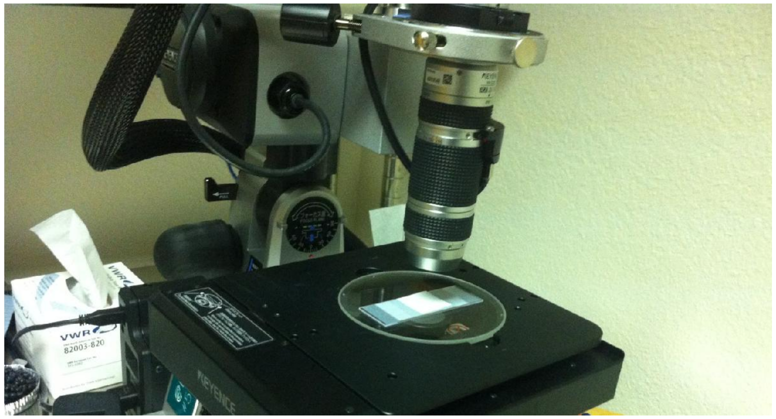
- All separators showed an increase in resistance under compression conditions.
- 9µm filled separator showed lower resistance after compressing at 590PSI, 80°C than the other PE separators without any compression.

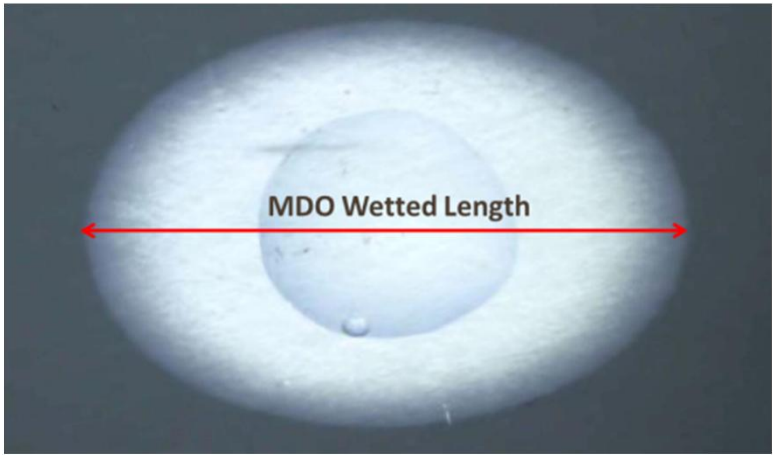
ELECTROLYTE WETTING

Droplet Wetting Method:

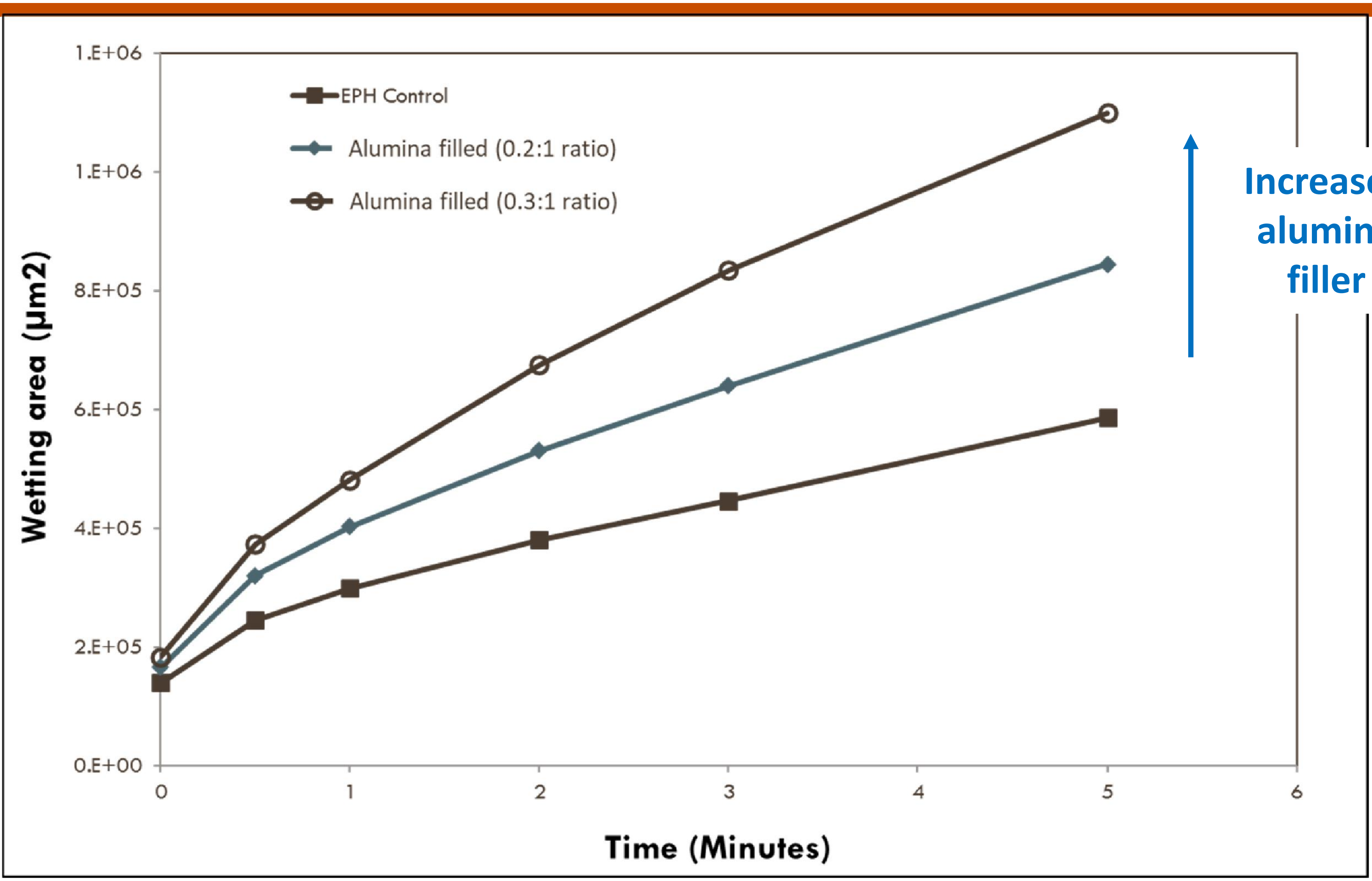
- Separator suspended in air to prevent solvent wicking on glass
- 5ul droplet placed on separator by micro-pipette. Wetted area measured after 5 minutes.
- Solvent: propylene carbonate/tri(ethylene glycol) dimethyl ether = 1/1 (vol.)







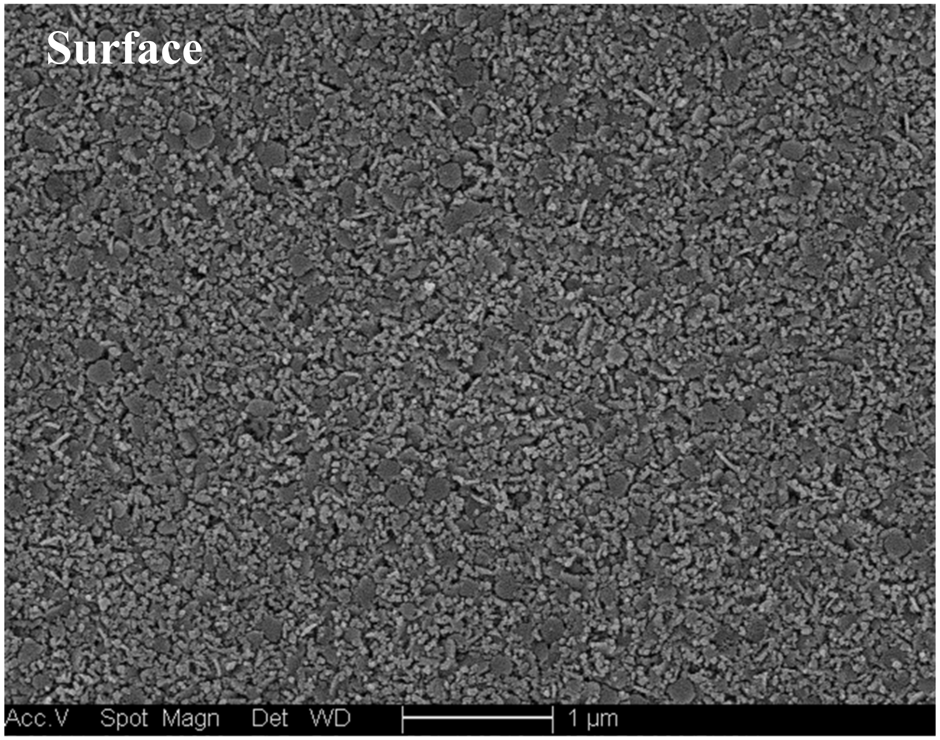
ALUMINA FILLED SEPARATOR SHOWS FASTER WETTING

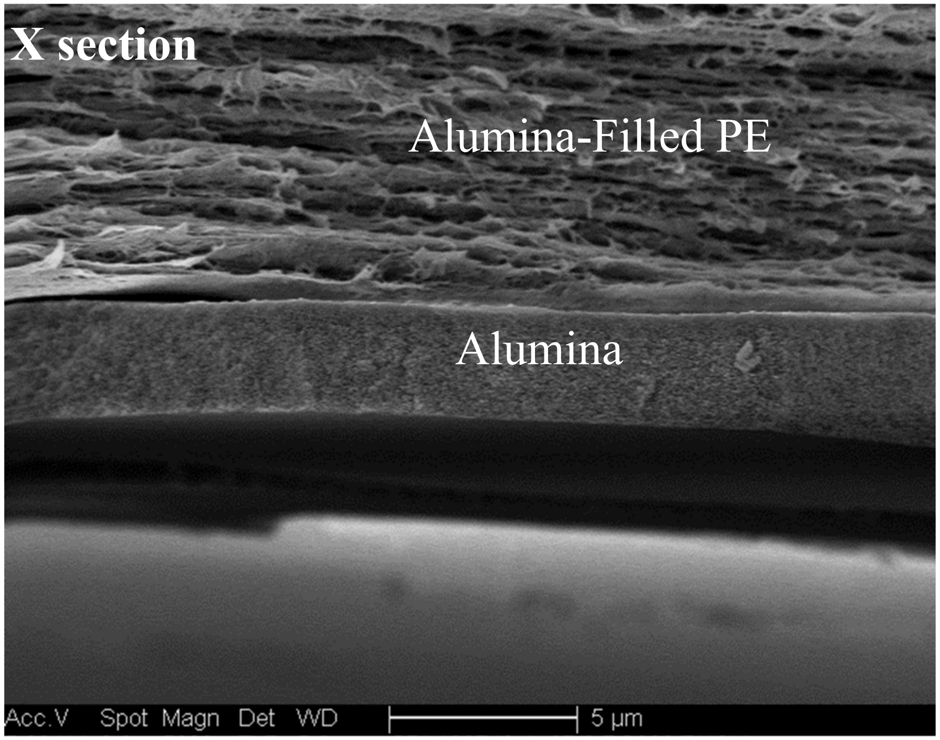


Increased alumina filler

Inorganic filled separator showed a ***substantial improvement in wetting*** compared to microporous PE control.

SEM: CERAMIC-COATED + CERAMIC-FILLED SEPARATOR





Initial results are promising for rechargeable Li metal batteries
- Ceramic filler improves wetting & filling of all available pores
- Nanoparticle coating serves as dendrite barrier

SUMMARY

- Li-ion separator performance characteristics are determined through a combination of raw material selection for both the polymer and ceramic phases, along with the process conditions used to produce the finished separator.

- Simple assumptions about ceramic thickness or ceramic coat weight required to achieve high temperature dimensional stability cannot be applied universally to all PE base separators.

- ENTEK has developed a portfolio of ceramic-modified separators with unique characteristics that include ultralow impedance, high temperature dimensional stability, and outstanding melt integrity.

- ENTEK is focused on delivering a strong value proposition to its partners while delivering the expected battery performance through separator engineering & design