PB-ACID BATTERY SEPARATORS

OXIDATION PATHWAYS AND THERMOMECHANICAL PROPERTIES

C. La, C. Rogers, R. Waterhouse, E. Hostetler, W. Wood, Sutaryo, D. Silvana, H. Hermawan, M. Ulrich, R. Towns, C. Beutelschies, and R.W. Pekala

ENTEK International LLC
ENTEK International LTD
PT ENTEK Separindo Asia

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22-24 SEPTEMBER

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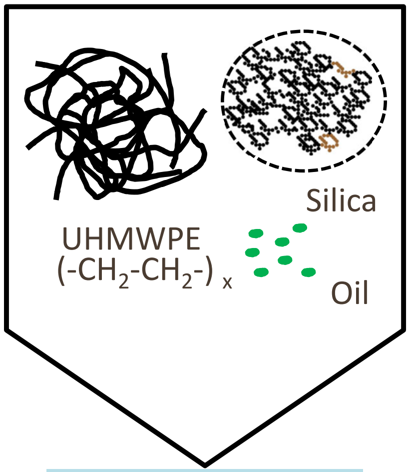
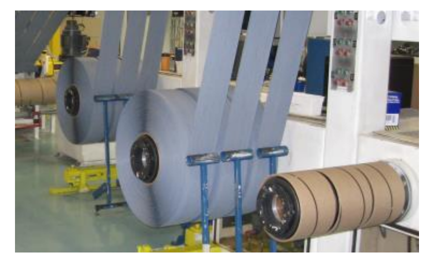
RAISING EXPECTATIONS. KEEPING THEM THERE.

KEY RAW MATERIALS AND SEPARATOR MANUFACTURING PROCESS



Extrusion → Calender → Extraction → Drying → Hot Air Oven → Slit & Wind →



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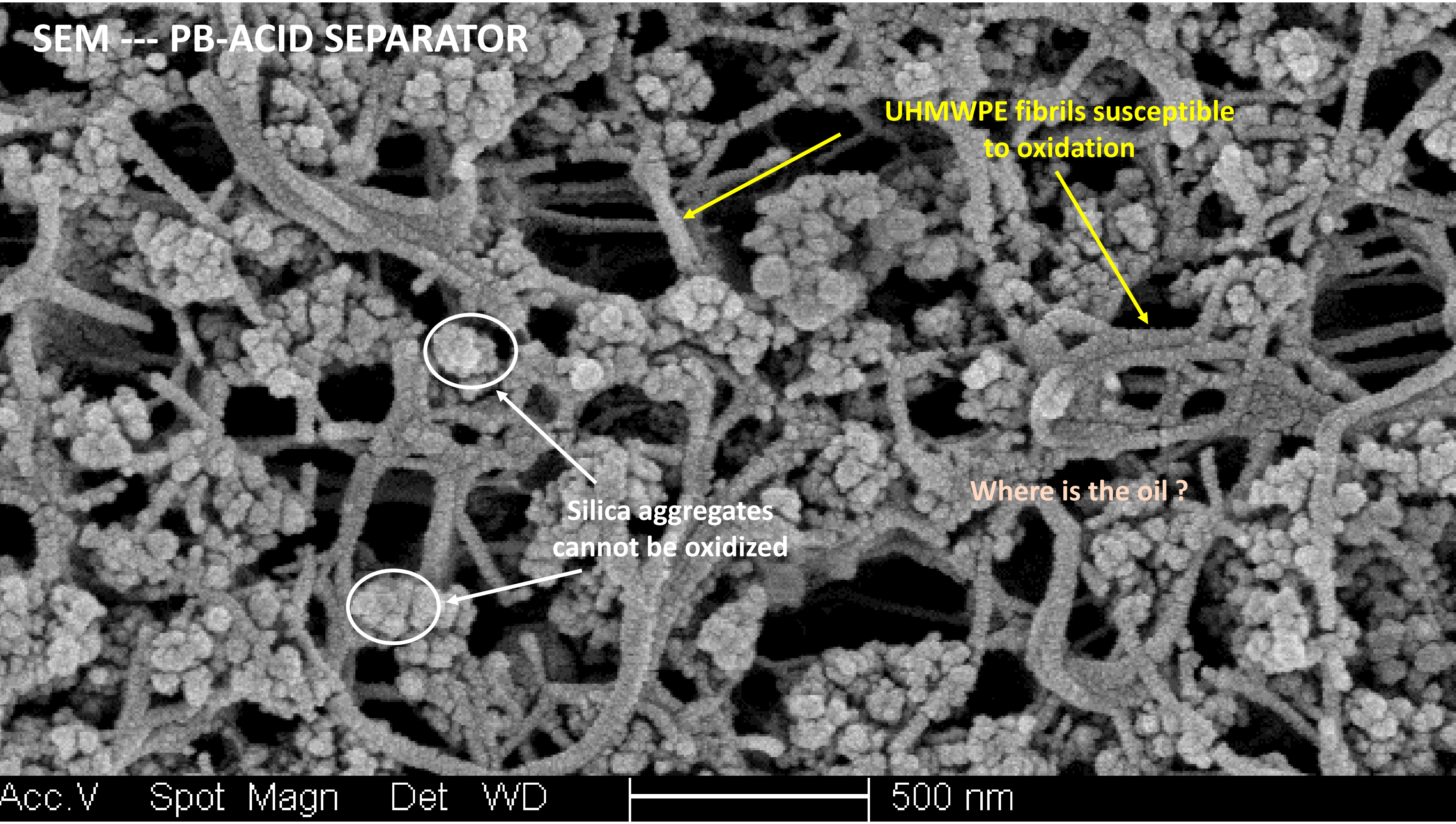
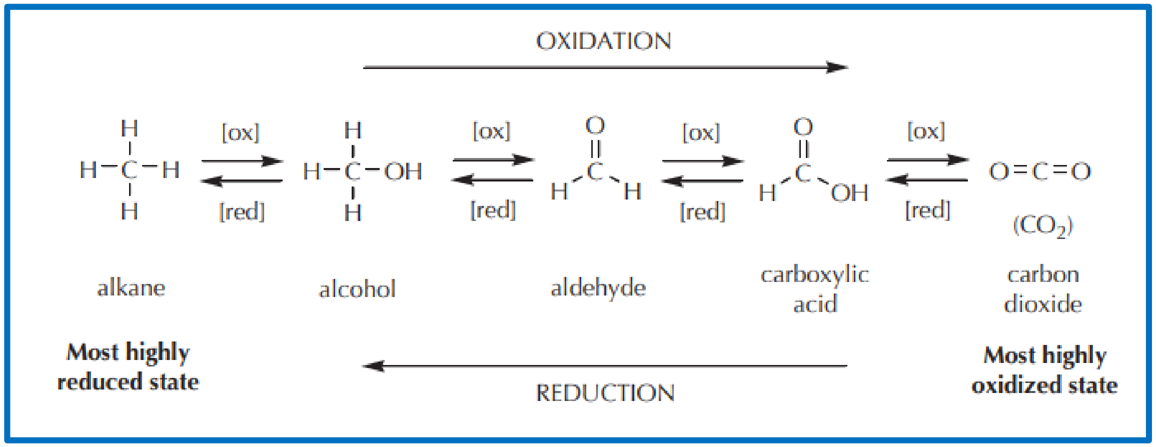
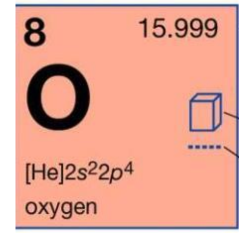

SEM --- PB-ACID SEPARATOR
UHMWPE fibrils susceptible to oxidation
Silica aggregates cannot be oxidized
Where is the oil ?
Acc.V Spot Magn Det WD
500 nm

UHMWPE AND OXIDATION RESISTANCE





1. The ***UHMWPE polymer is responsible for the mechanical integrity*** of battery separators (i.e., puncture strength, flexural modulus, % elongation, tensile strength), but ironically, it is also susceptible to oxidation

2. If the ***UHMWPE undergoes chain scission or crosslinking when attacked by oxygen***, the elongation of the separator will be reduced.

3. As such, a small amount of ***process oil is purposefully left behind in separators so that it can be preferentially oxidized to protect the UHMWPE polymer***

4. The ***oxidized oil will often be solubilized into battery acid*** and subsequently converted to CO2 and H2O.

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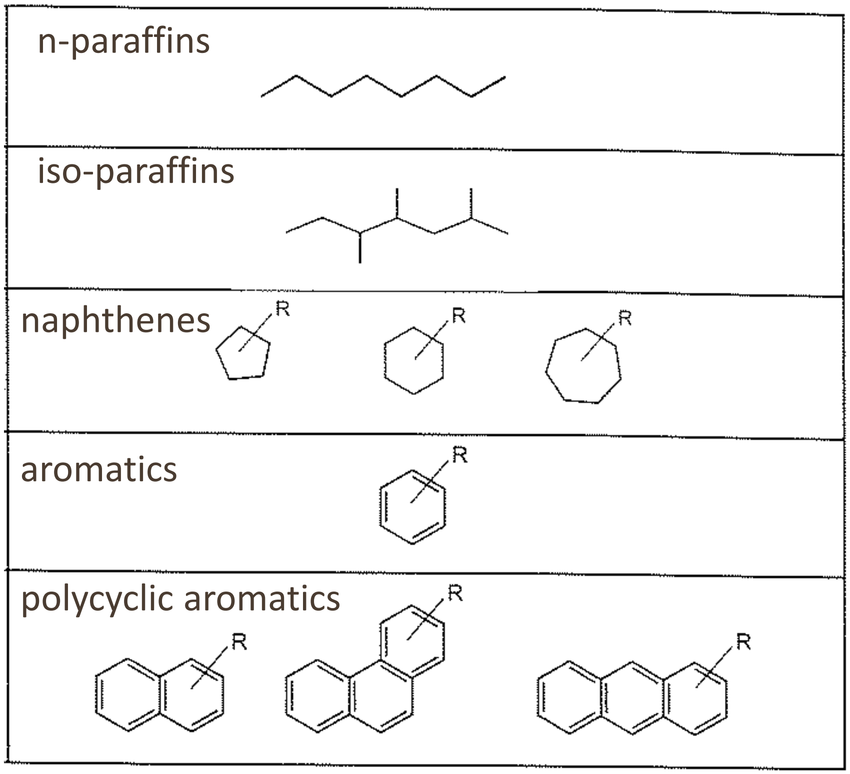
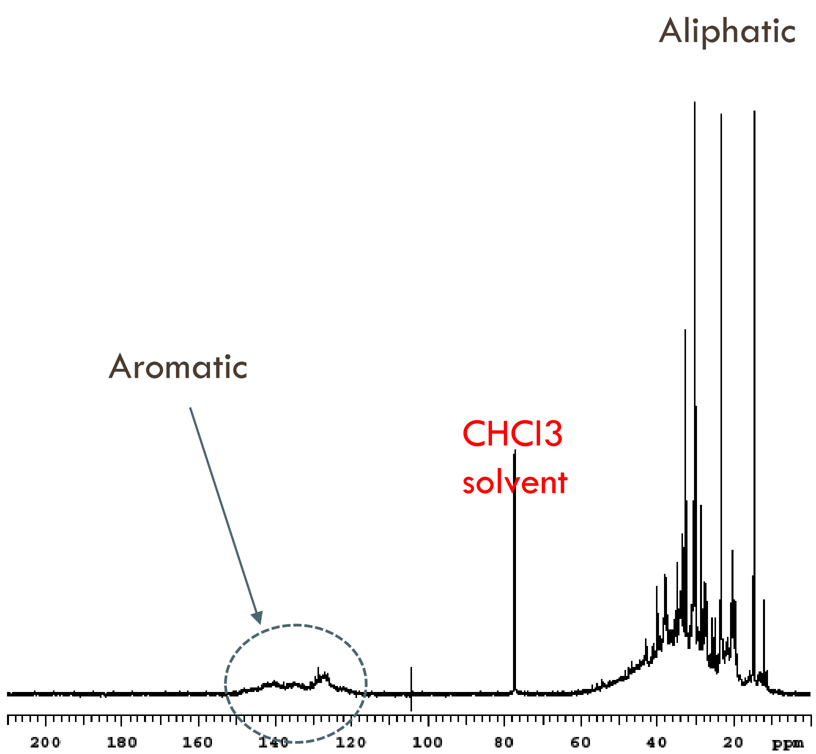
PROCESS OILS ARE COMPLEX CHEMICAL MIXTURES





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THERMAL OXIDATIVE DEGRADATION

- Chemical composition
  - SiO2/PE ratio
  - % residual oil
  - process oil

- Physical properties
  - MD elongation
  - % crystallinity

- Test methods
  - **Hydrogen peroxide in sulfuric acid (Perox 80)**
  - Potassium dichromate in sulfuric acid
  - Heated sulfuric acid
  - **Simulated electrochemical oxidative condition in battery cell under charging**
  - Oxidation induction time
  - High temperature battery life test

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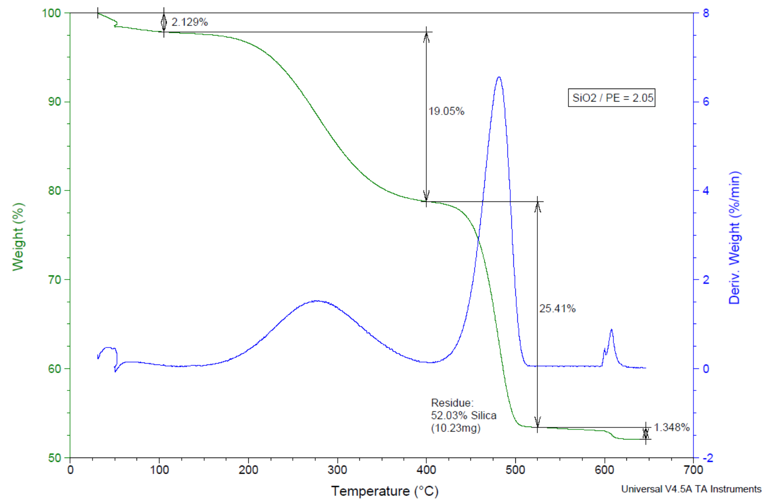
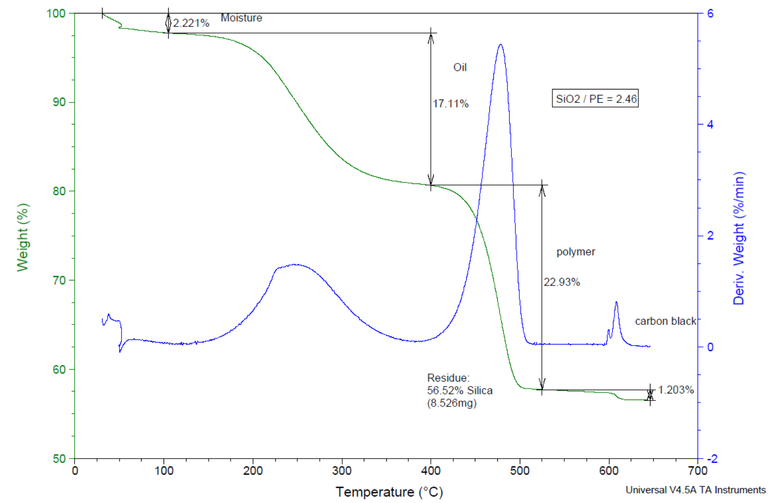
TEST SAMPLES

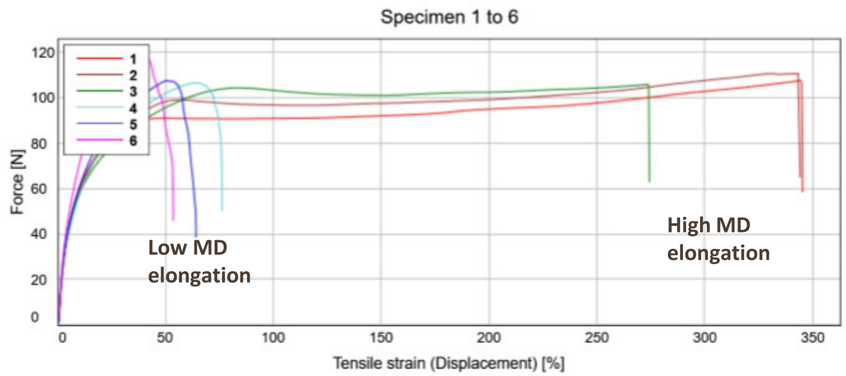
	SiO_2/PE ~ 2	SiO_2/PE ~ 2.5
High MD elongation > 250%	**2 H**	**2.5 H**
Low MD Elongation < 100%	**2 L**	**2.5 L**

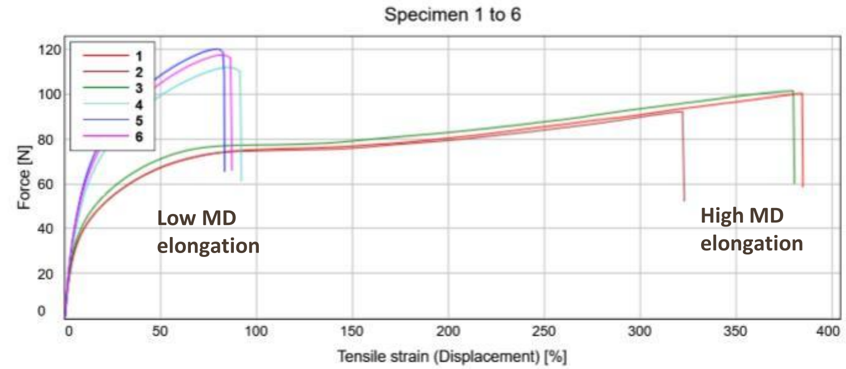
- ALL samples have been manufactured with the same process oil and UHMWPE grade
- Residual oil content 16-20%
- Oil/PE mass ratio 0.75 – 0.85
- 57-62% porosity

TGA AND MECHANICAL PROPERTIES

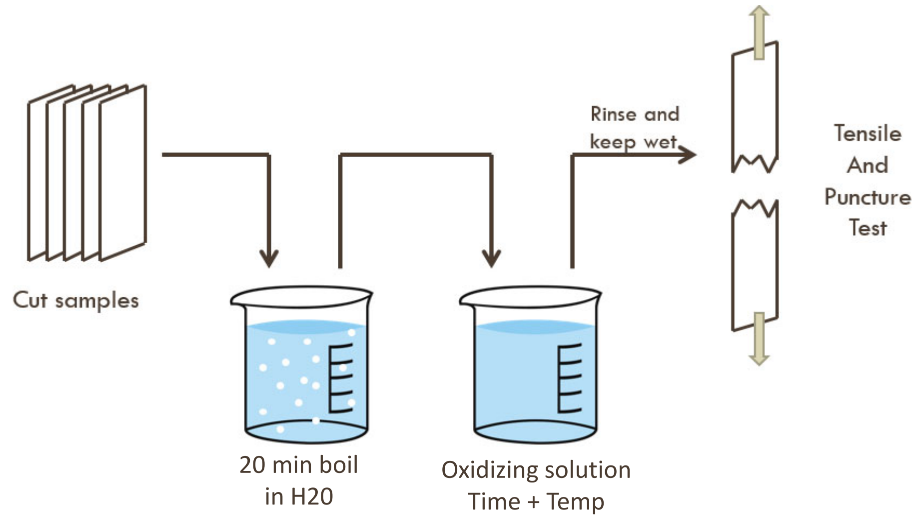


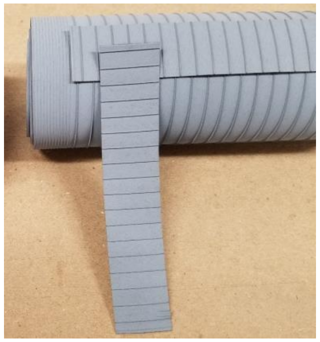


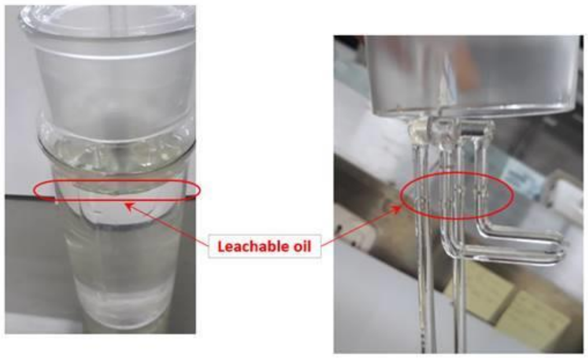


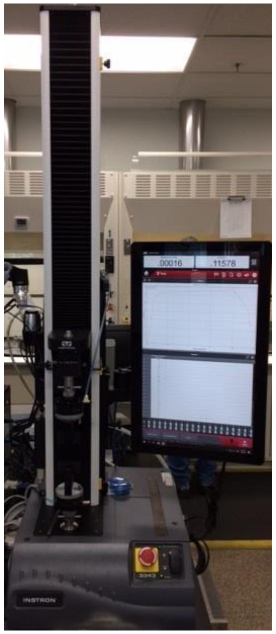


TEST PROCEDURE AND SET-UP

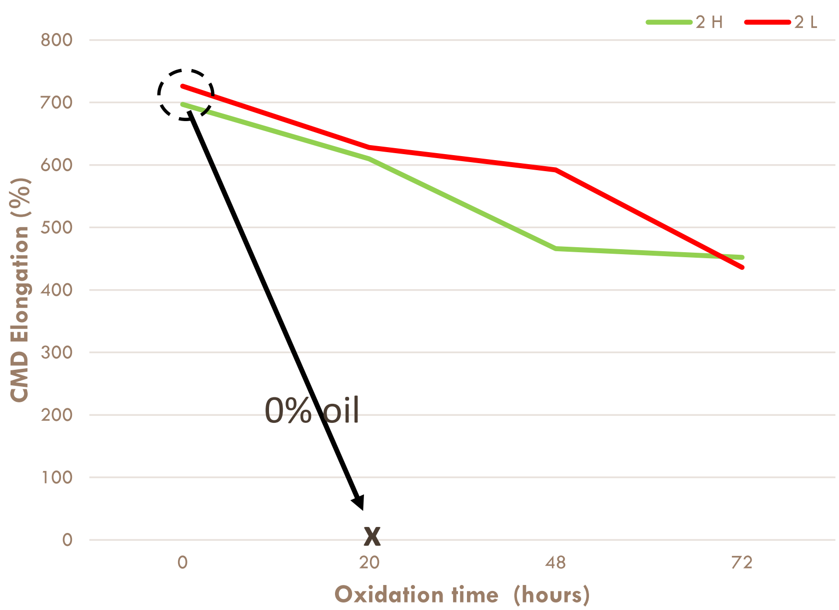


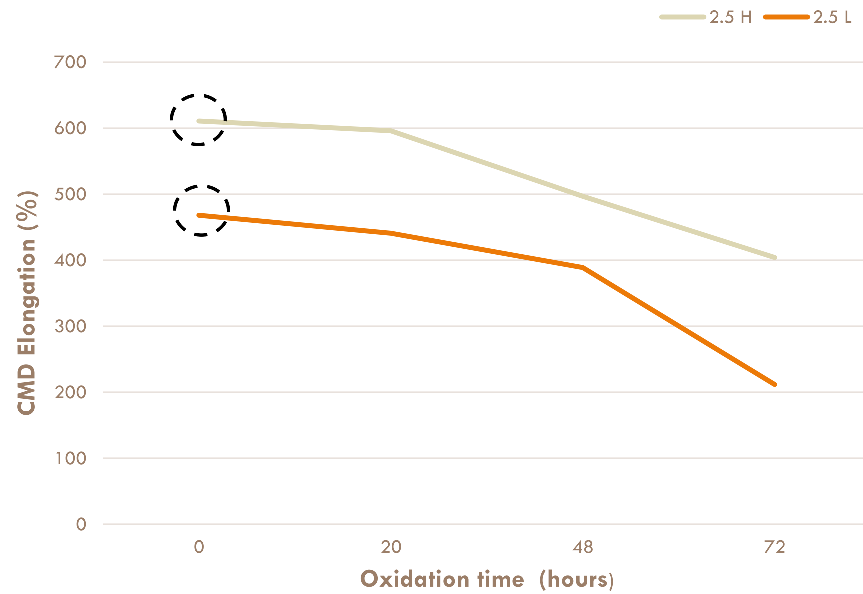






PEROX 80 --- CMD ELONGATION (ABSOLUTE VALUES)





Data were averaged from 10 samples each for every oxidation time period

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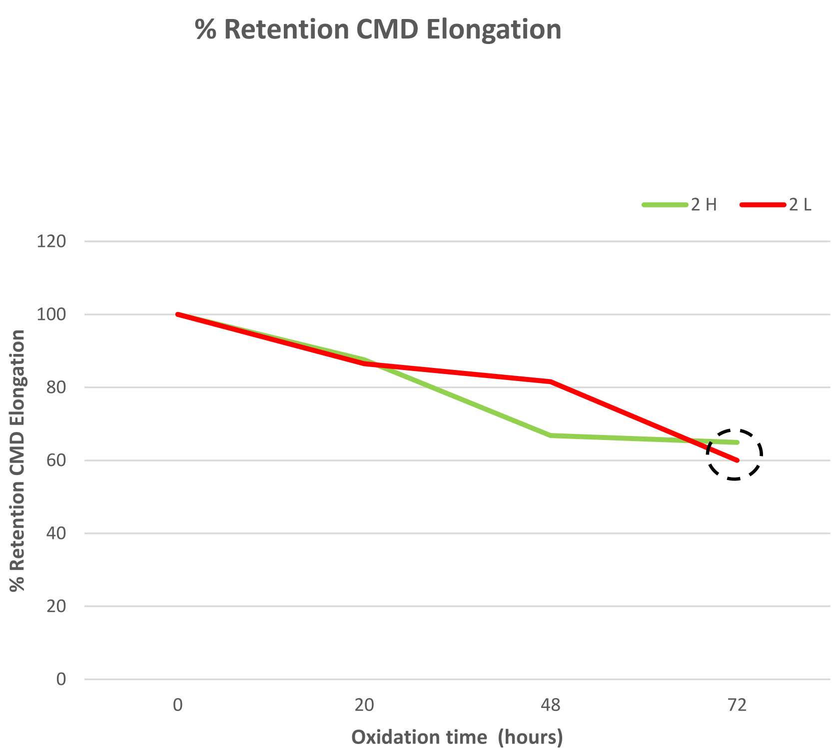
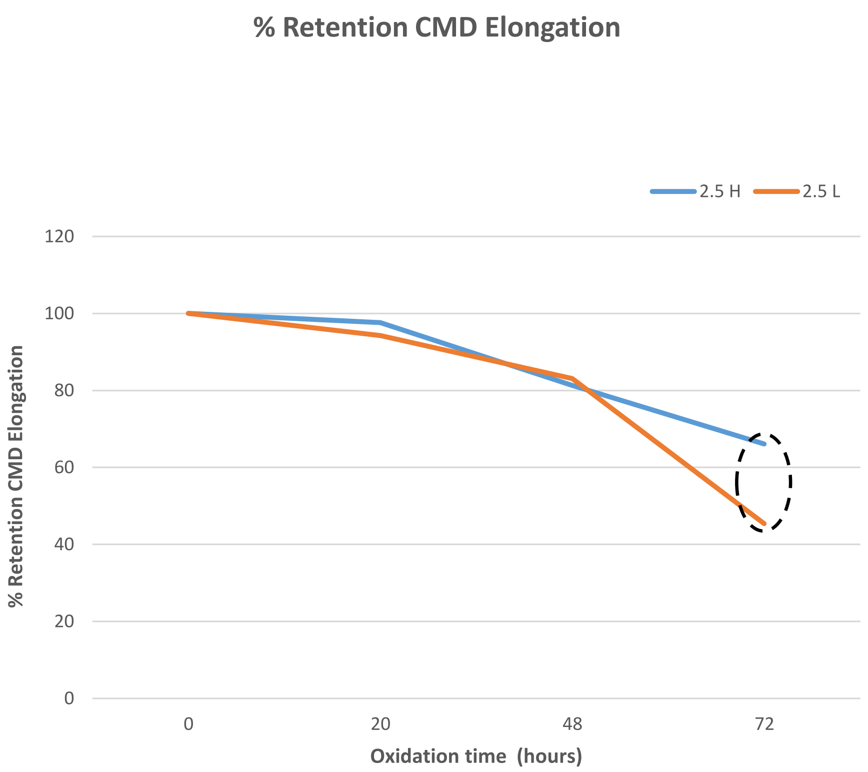
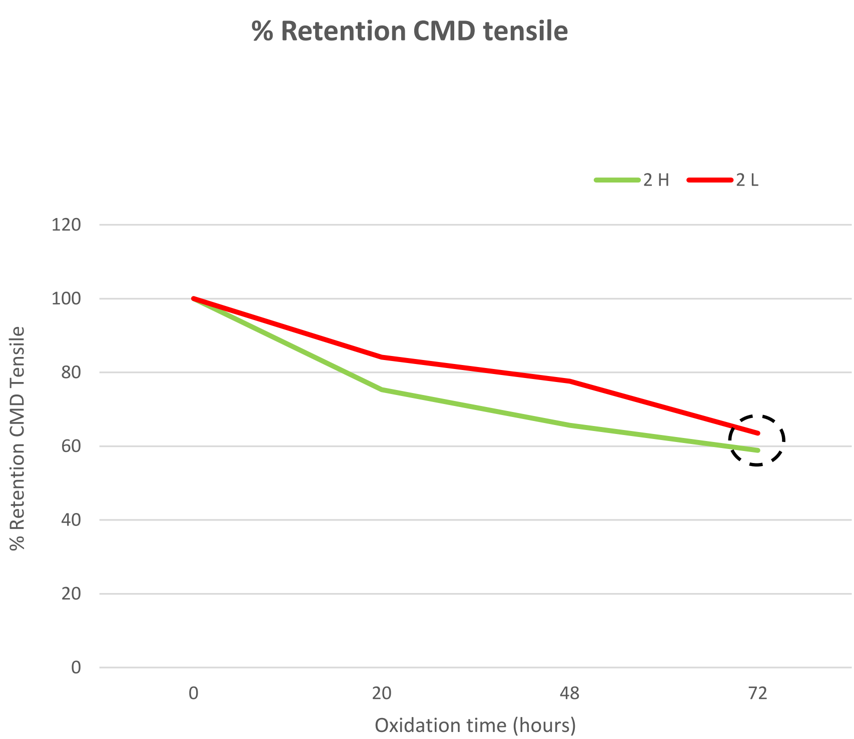
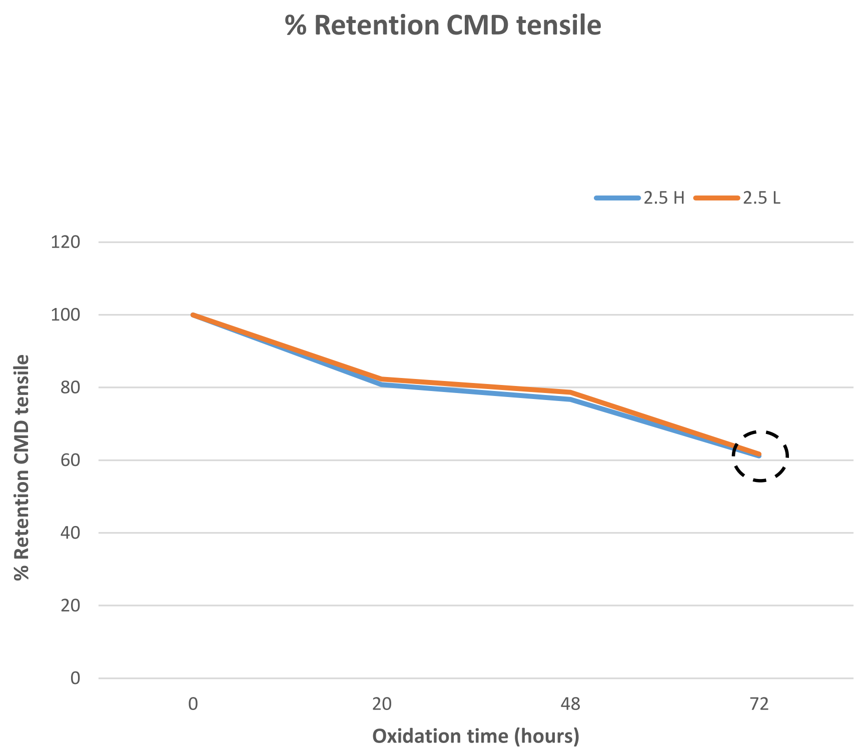
PEROX 80 --- CMD ELONGATION



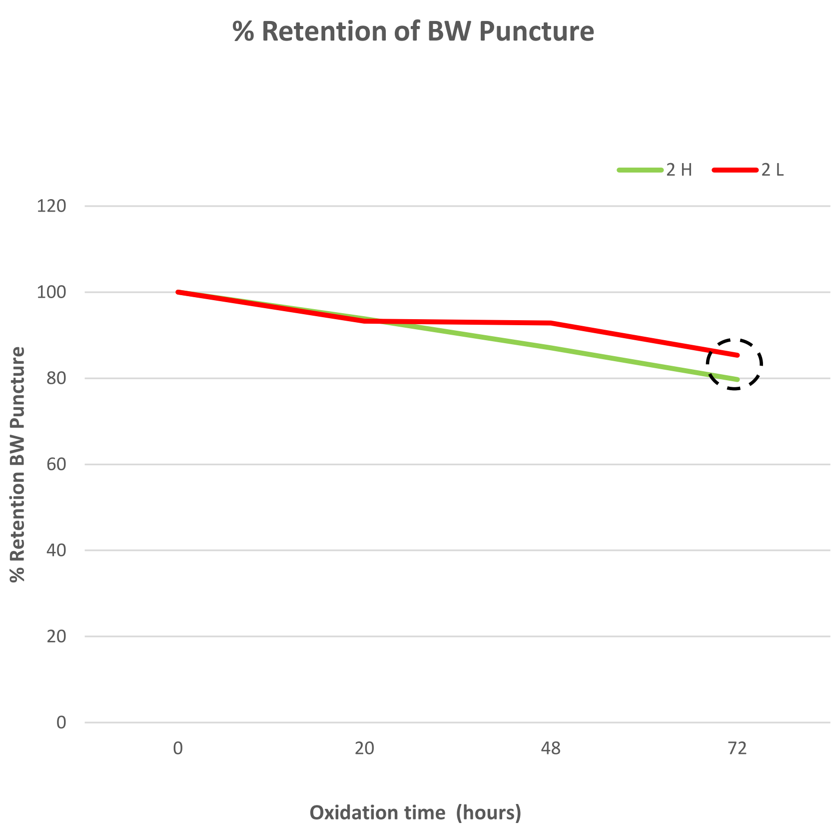


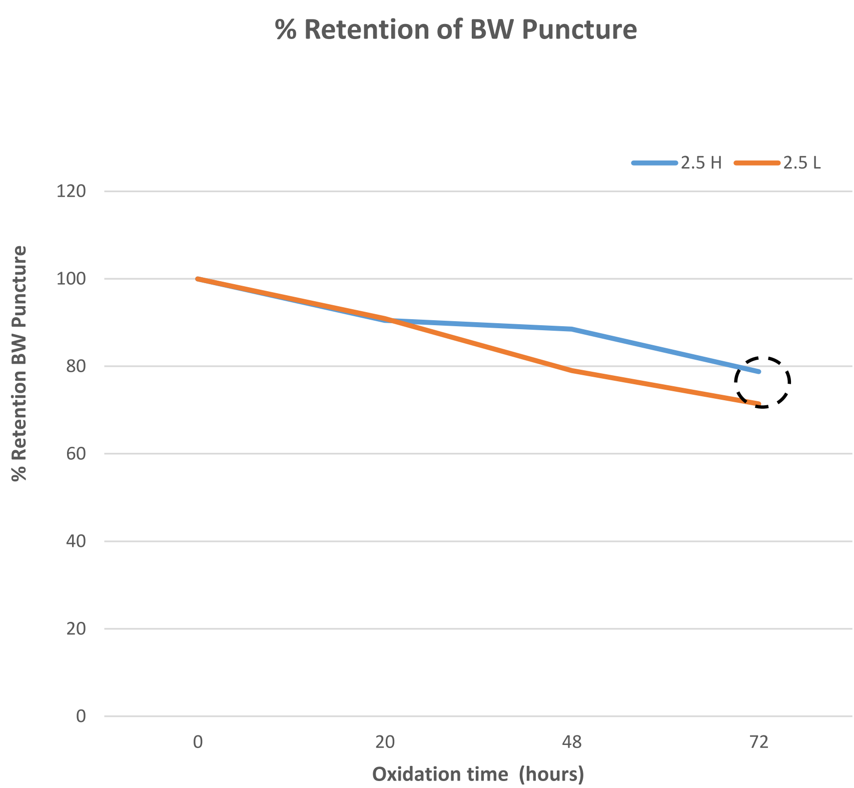
PEROX 80 --- CMD TENSILE STRENGTH



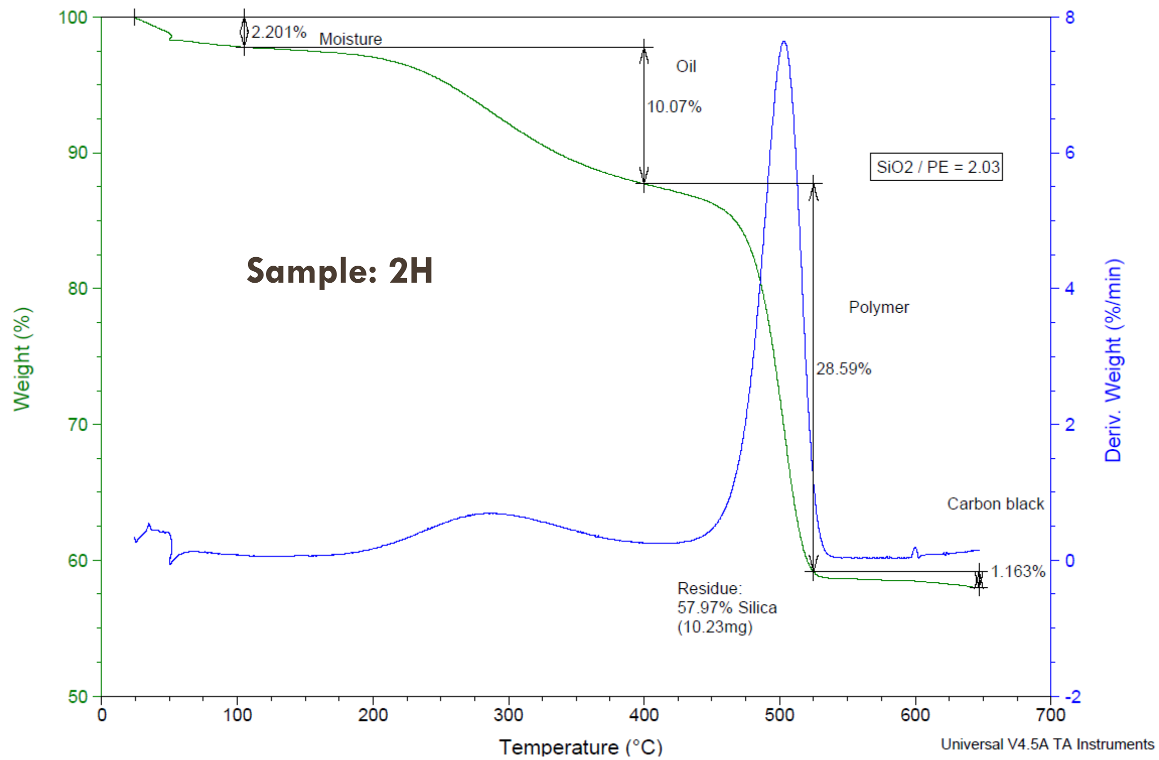


PEROX 80 --- PUNCTURE RESISTANCE





TGA ANALYSIS AFTER 72 HR PEROX 80 TEST



Sample ID	Oil Content (%) Initial	Oil Content (%) After 72 hr Perox 80
2 H	20.6	10.1
2 L	19.0	9.6
2.5 H	18.3	8.9
2.5 L	17.1	8.0

- Takeaways
  - ~ 50% of residual oil is consumed during 72 hr Perox 80 test
  - The degradation rate was similar for all 4 separator families because they have same oil, UHMWPE, and similar Oil/PE ratios
  - High MD elongation separators exhibit (1) greater toughness (energy to rupture) and (2) equivalent or better oxidation resistance than low MD elongation separators

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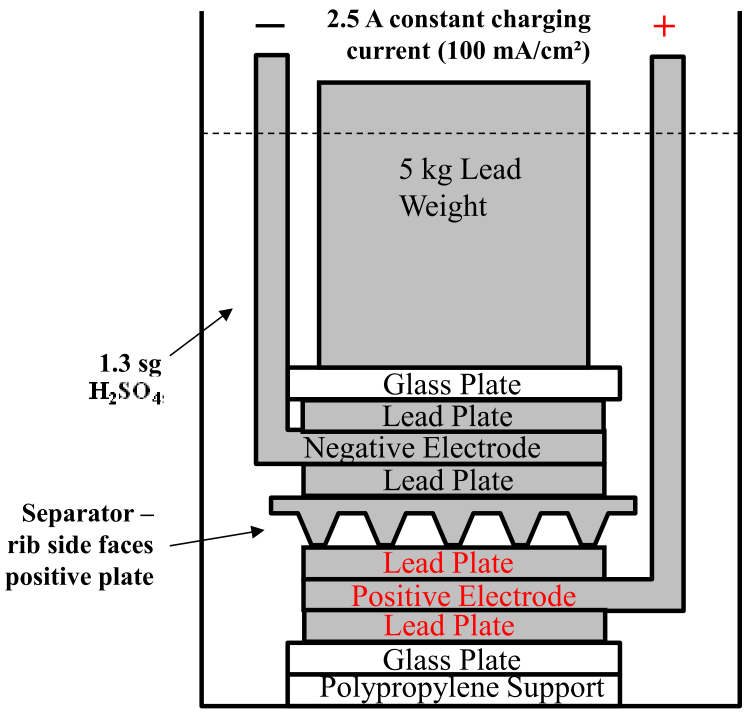
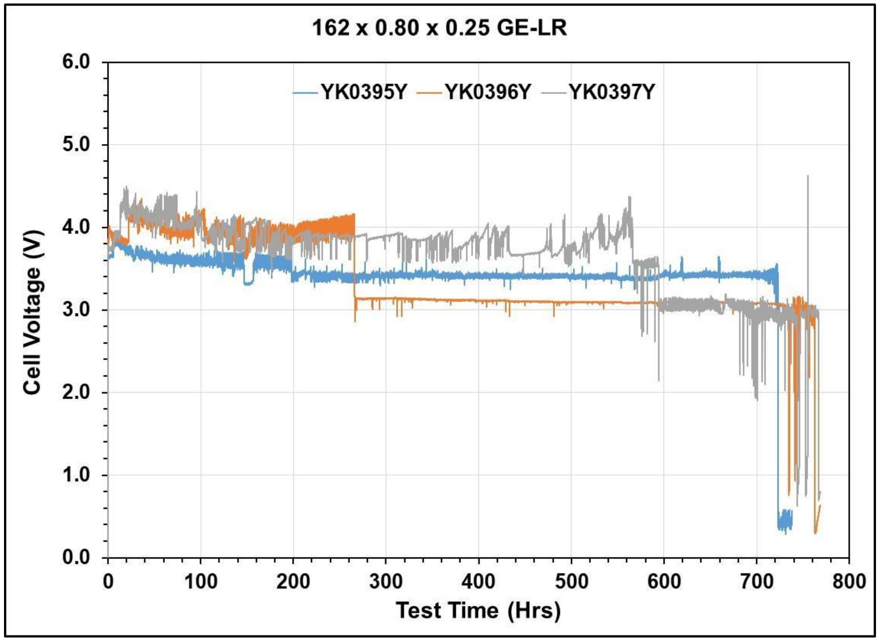
ELECTROCHEMICAL OXIDATION TEST PROCEDURE

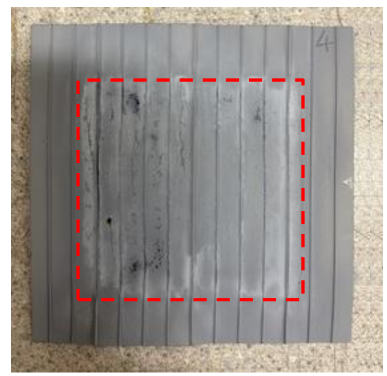


- Originated from Japanese National Railways; modified by Japanese battery manufacturer
- 7 x 7 cm^2 separator sample is placed with the rib side facing positive plate.
- The cell stack is assembled inside a 2000 mL glass beaker filled with 1.3 sg H_2SO_4, maintained at elevated temperature in a water bath:
  - 5kg lead weight is placed on top of the cell stack
- The cell is overcharged with a 2.5 A constant current (100 mA/cm^2):
  - Test is terminated when $\frac{\Delta V}{\Delta t} > 0.2V/min$

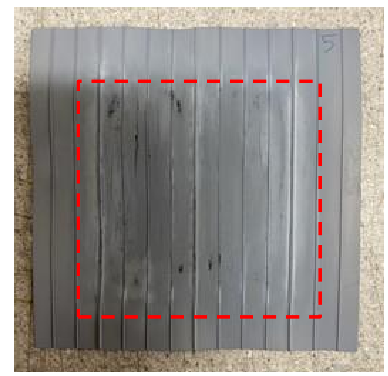
LR SEPARATOR – 0.25 MM BW



Test ID	Time to Failure (hrs)
YK0395Y	720
YK0396Y	735
YK0397Y	682
Avg.	712



YK0395Y: After test termination



YK0396Y: After test termination

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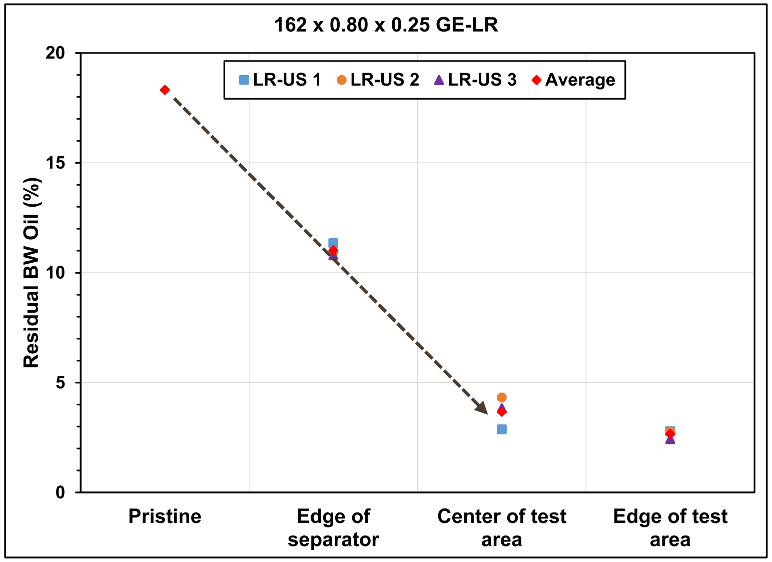
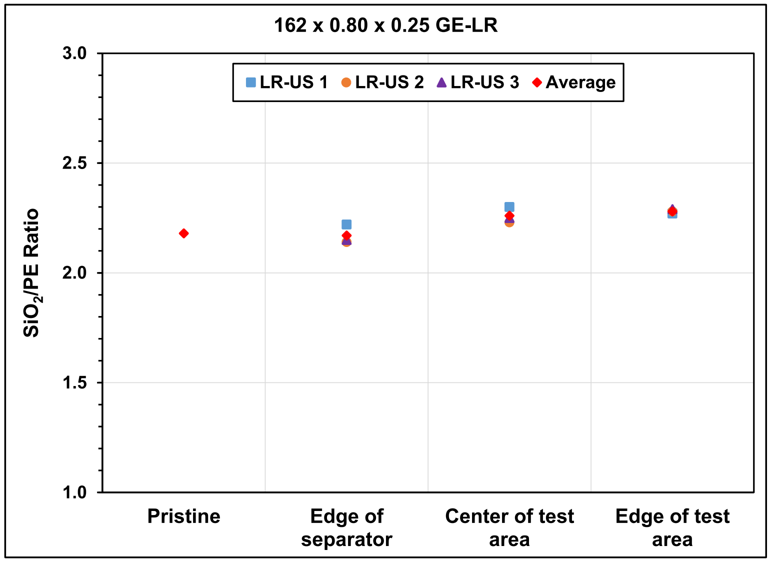
LR SEPARATOR --- COMPOSITIONAL CHANGES AFTER ELECTROCHEMICAL TEST

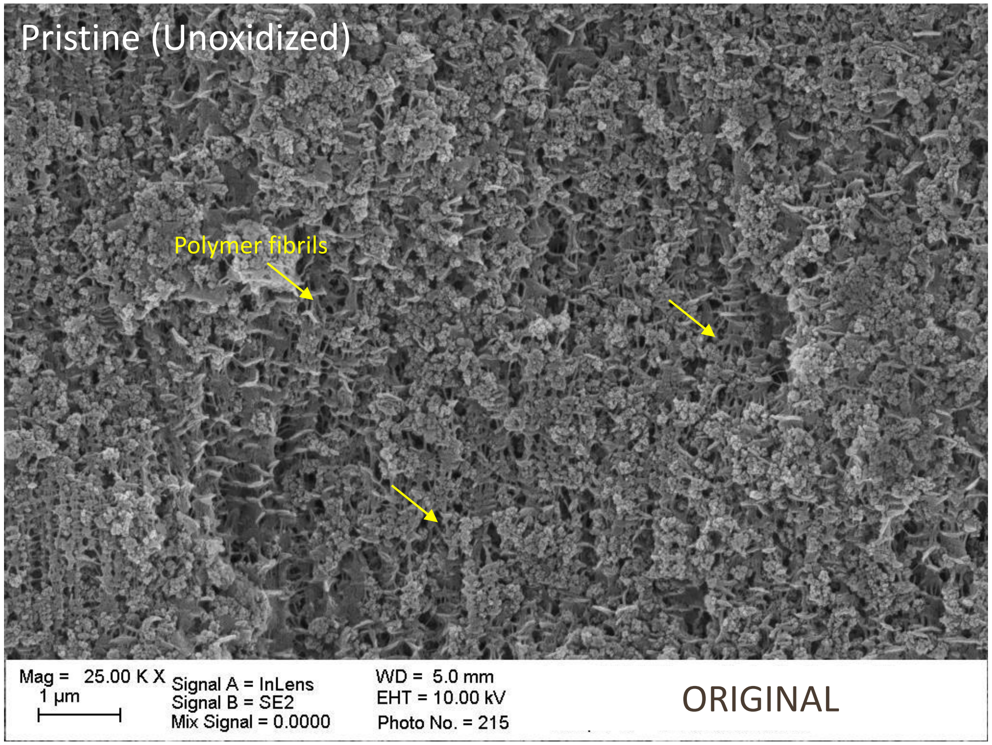


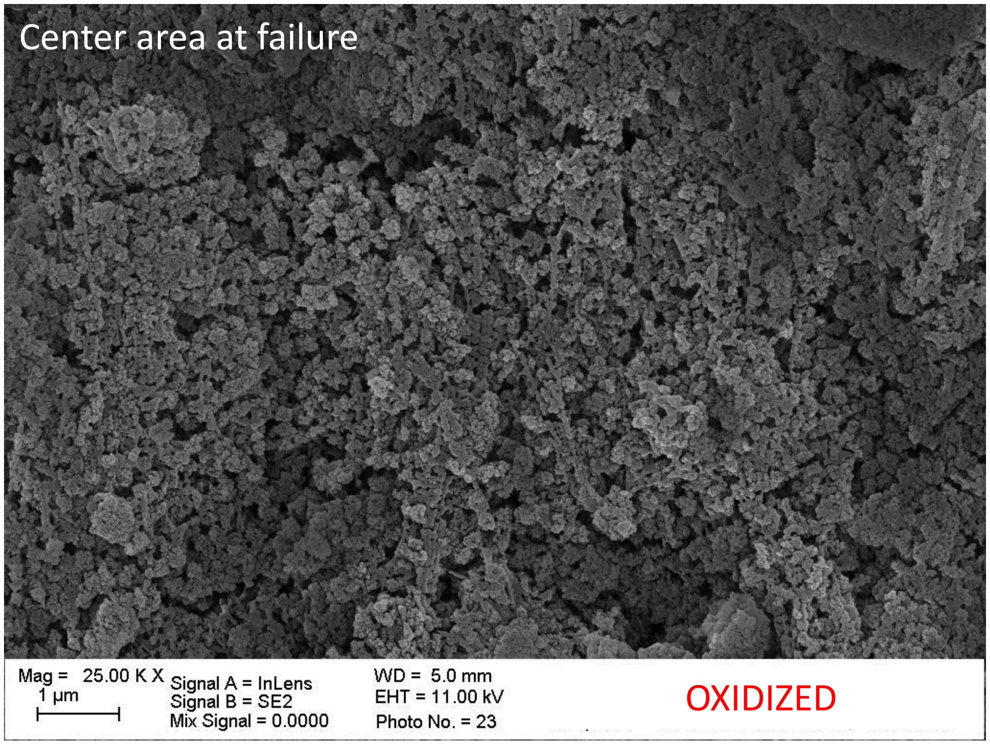


		Pristine		Edge of separator		Center of test area		Edge of test area	
Test ID	Test ID	BW Oil (%)	SiO2/PE	BW Oil (%)	SiO2/PE	BW Oil (%)	SiO2/PE	BW Oil (%)	SiO2/PE
LR-US 1	YK0395Y	18.32	2.18	11.34	2.22	2.87	2.3	2.79	2.27
LR-US 2	YK0396Y	18.32	2.18	10.94	2.14	4.32	2.23	2.78	2.28
LR-US 3	YK0397Y	18.32	2.18	10.79	2.15	3.83	2.25	2.44	2.29
Average	**Average**	**18.3**	**2.2**	**11.0**	**2.2**	**3.7**	**2.3**	**2.7**	**2.3**

All separators showed a significant reduction in oil content in the electrochemical test area

SURFACE SEM--- LR SEPARATOR





Separator surface is largely composed of silica after failure in the electrochemical oxidation test

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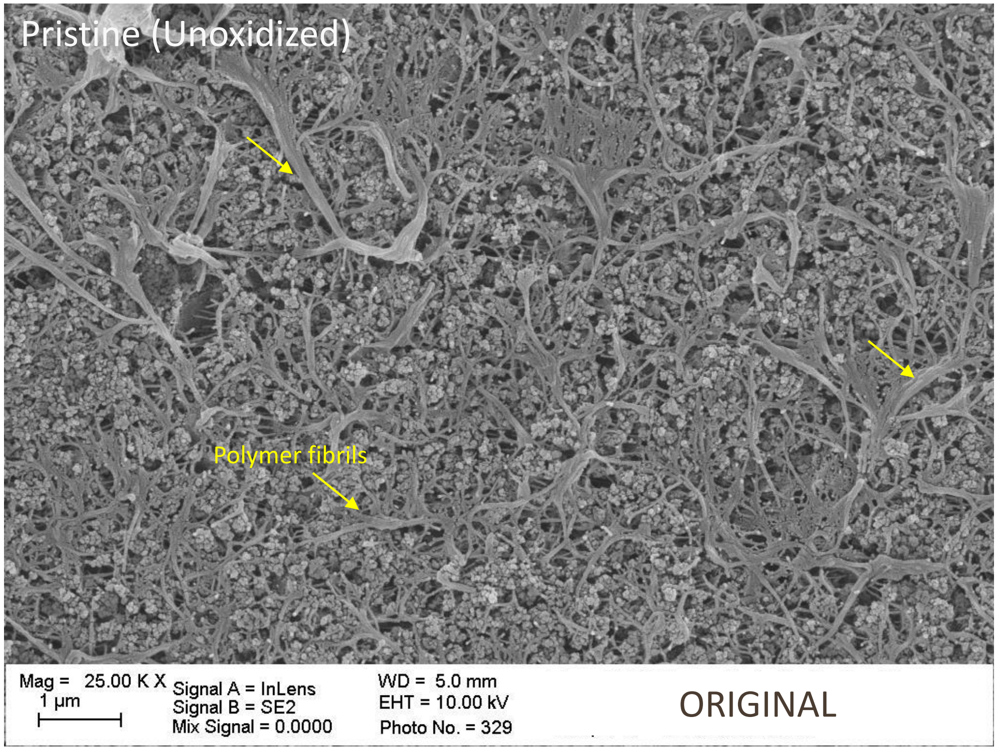
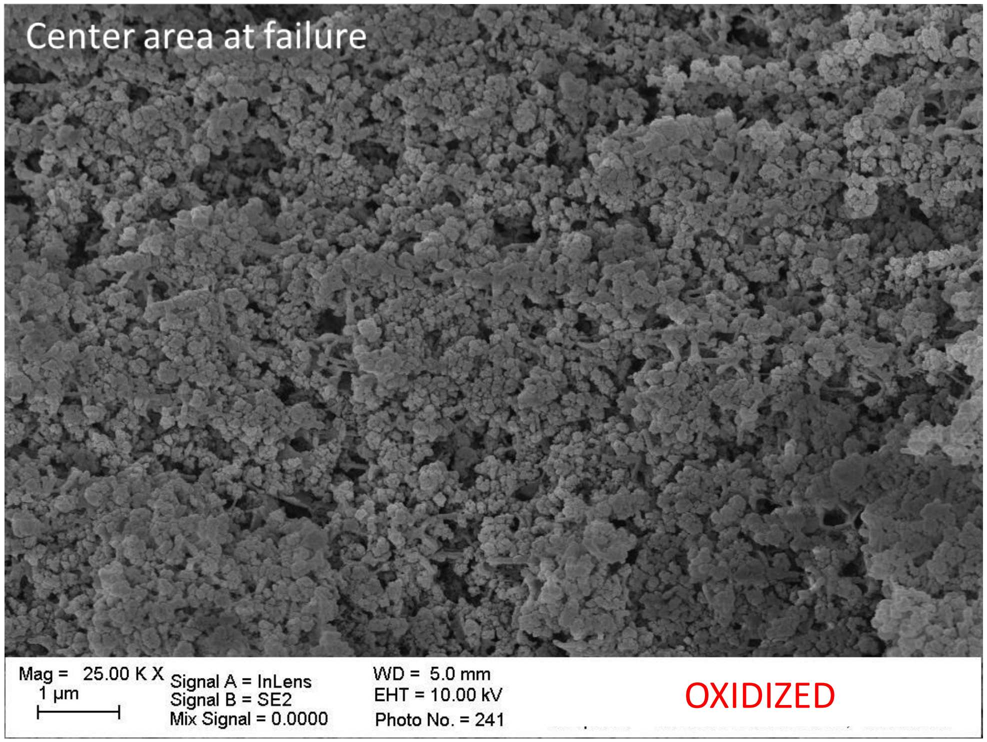
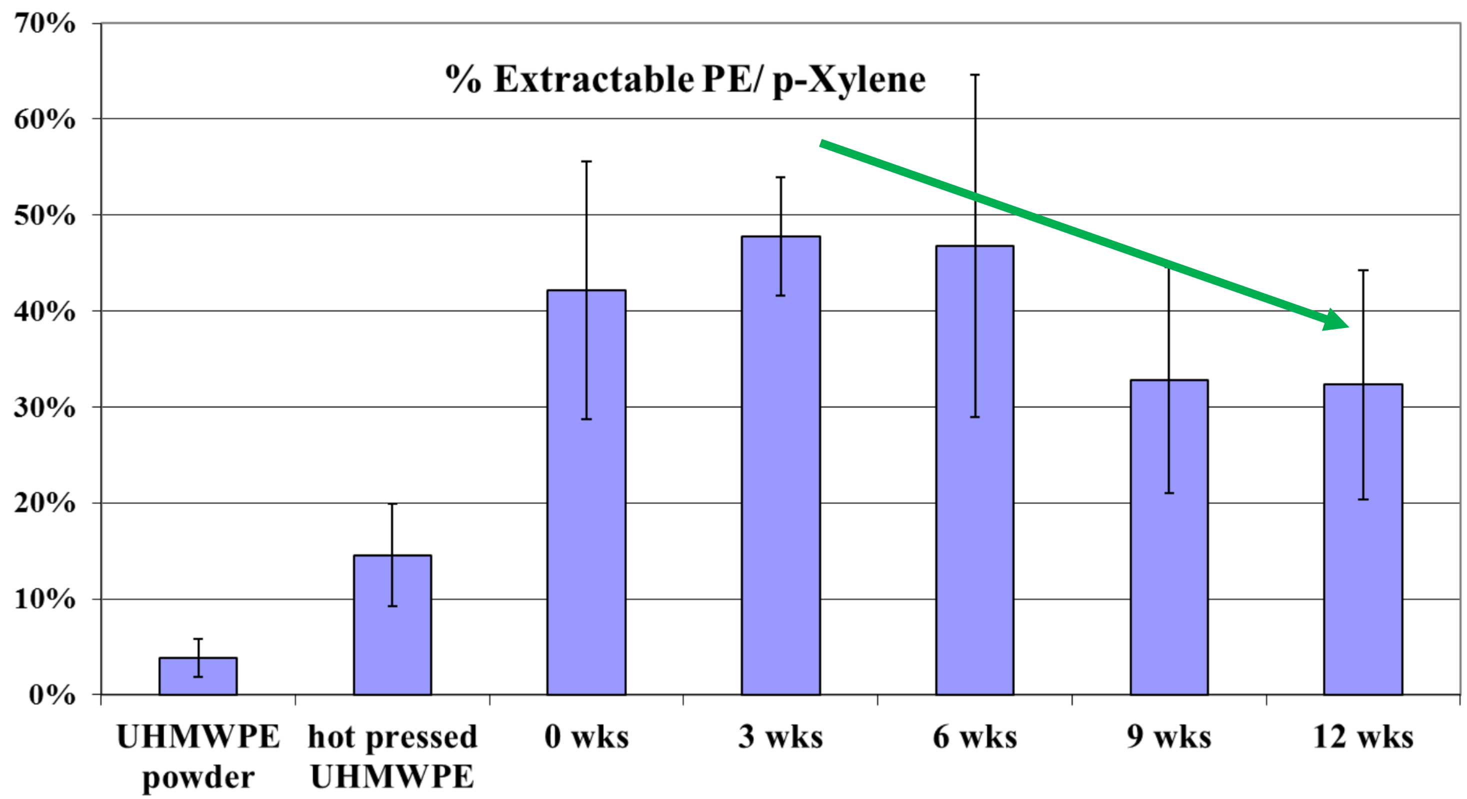
FRACTURE SEM--- LR SEPARATOR



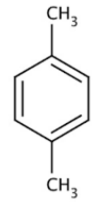


Note the lack of polymer fibrils after failure in the electrochemical oxidation test

CHAIN SCISSION VS CROSSLINKING IN BATTERY LIFE TEST



- Soxhlet extraction
  - Para-xylene
  - 138 °C



THERMOMECHANICAL ANALYSIS (TMA)

- TMA measures dimensional changes under controlled conditions of force, atmosphere, time, and temperature
- Changes in dimension are measured as the sample is heated
- Residual stresses in film samples are seen in the dimensional changes of the sample

Nitrogen purged furnace in open position

Film sample mounted in tension fixture

- All measurements in machine direction
- Positive change is elongation, negative change is shrinkage
- Y-axis is % change
- X-axis is temperature or time
- Method 1
  Ramp 10°/min to 40°, hold for 1 minute
  Ramp 10°/min to 80°, hold for 30 minutes
- Samples from Perox 80 study, except 2.5 LJ is from competitor with low MD elongation and SiO_2/PE ~ 2.5

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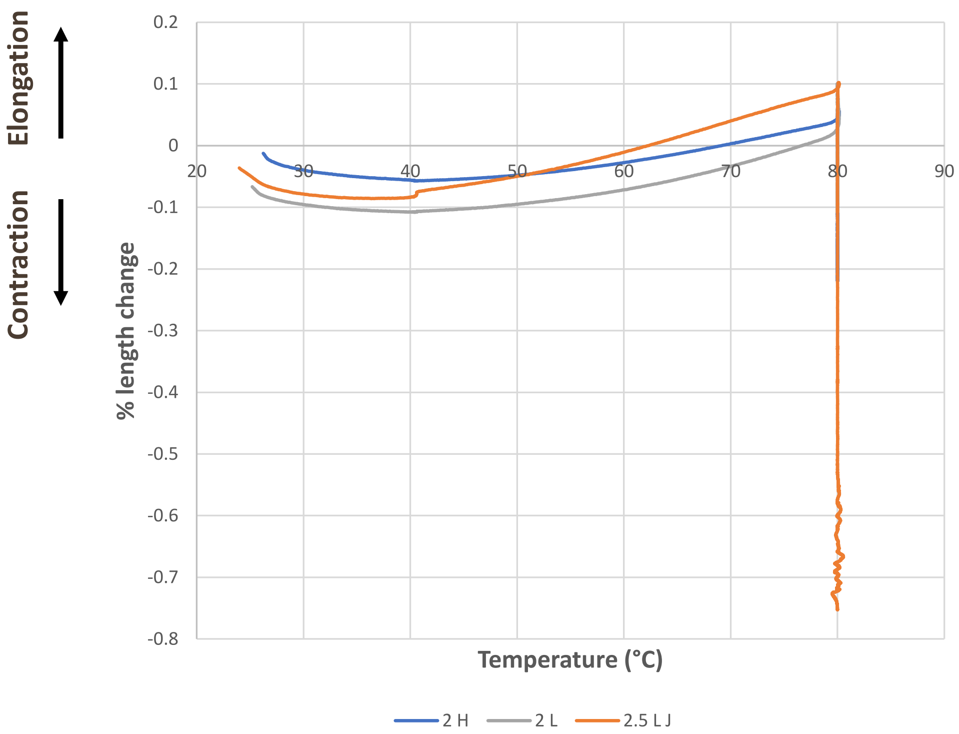
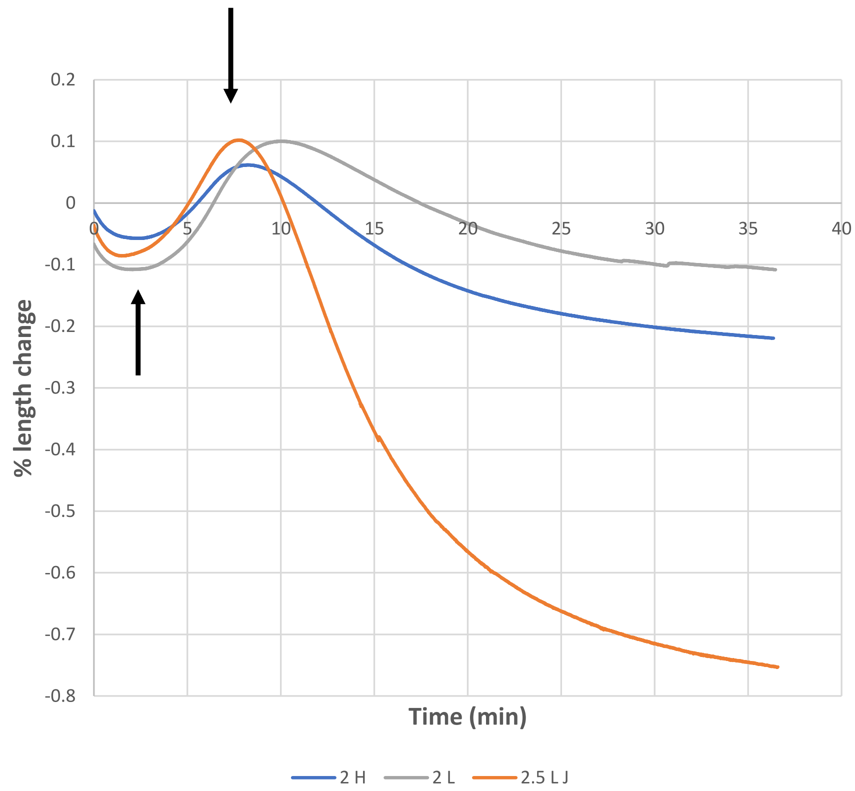
SEPARATOR TMA --- AS PRODUCED





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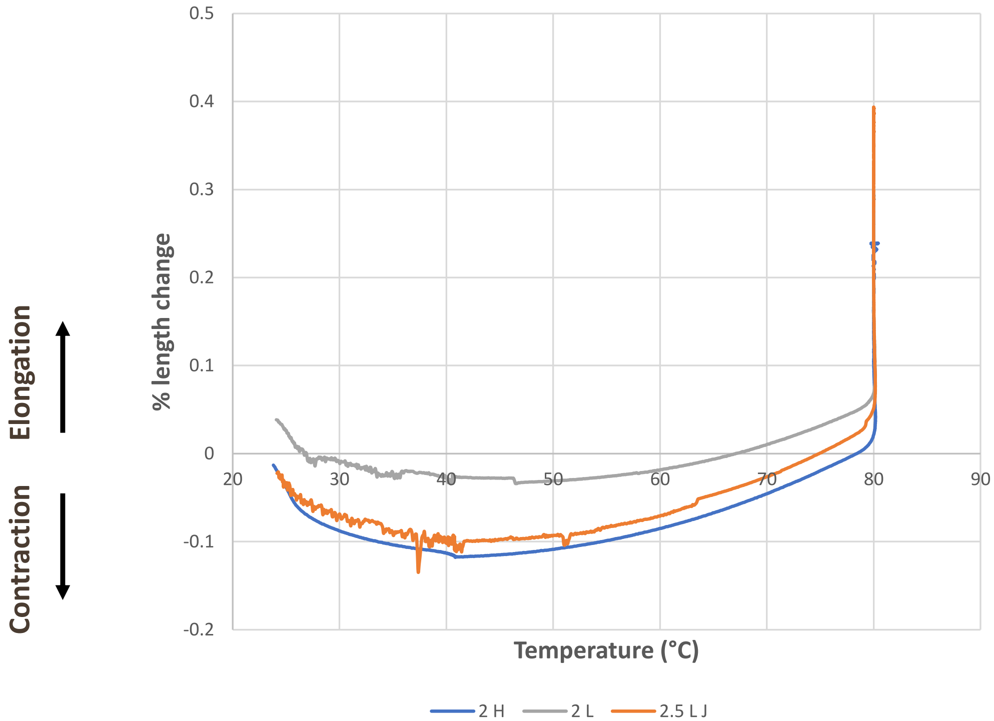
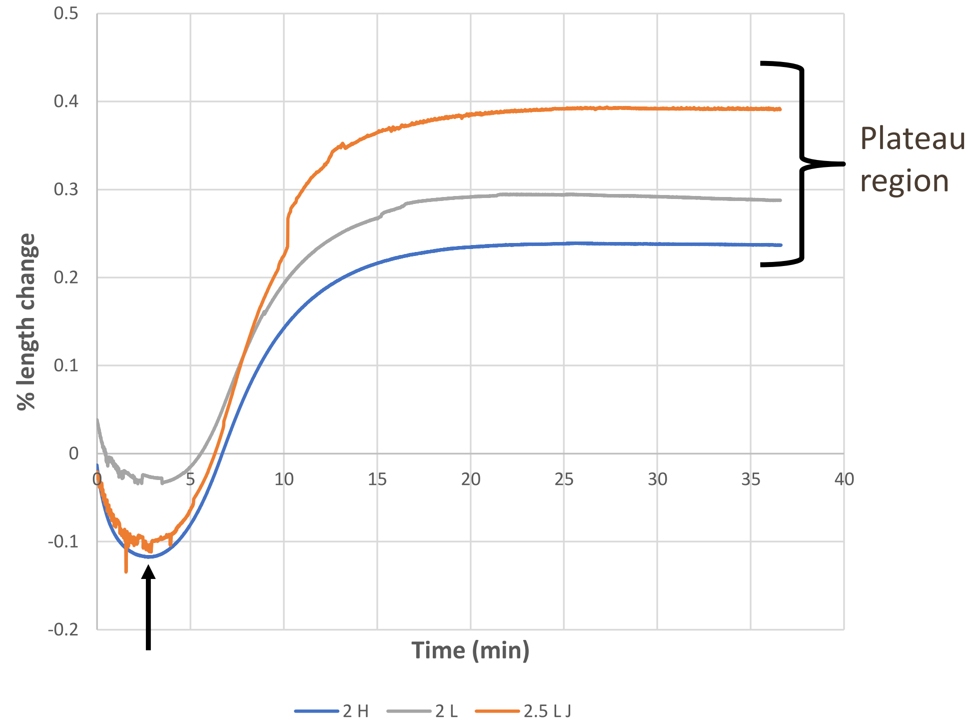
SEPARATOR TMA --- EFFECT OF THERMAL HISTORY





Samples were boiled in water for 30 mins and then dried in oven at 110 C

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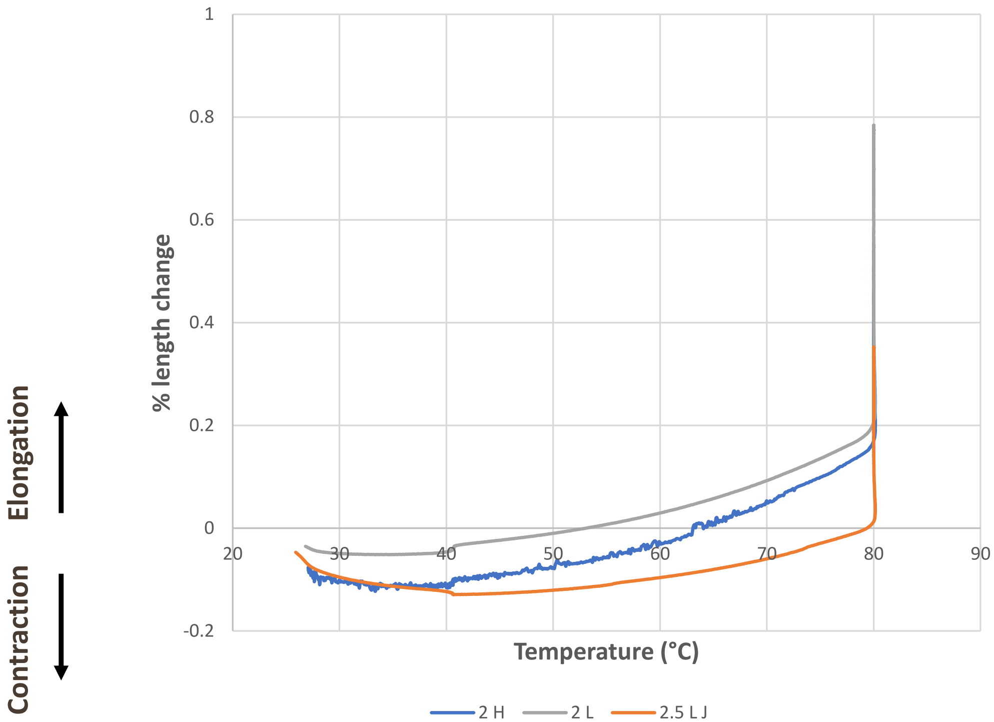
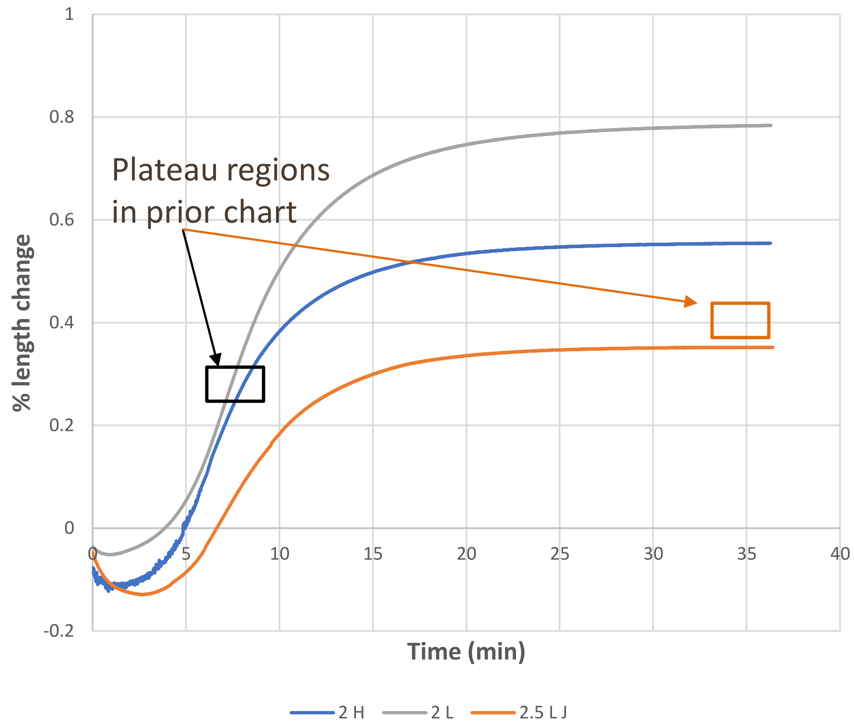
SEPARATOR TMA --- AFTER PEROX 80





Samples were boiled in water for 30 mins, exposed to Perox 80 solution for 20 hours, washed in water to neutral pH, and then dried at 110 C

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SUMMARY

- PE/SiO2 separators will always be susceptible to oxidation in Pb-acid batteries.
- ENTEK is utilizing thermal analysis tools (TGA, TMA, DSC) combined with chemical analysis (NMR, IR) to gain insights about the thermal oxidative degradation of PE/SiO2 separators.
- Mass loss from separators exposed to oxidizing solutions gives an incomplete picture of separator degradation since residual oil is reacted or consumed as part of the mechanism for protecting the mechanical integrity of a separator
- Controlling the ***amount*** and ***composition*** of residual process oil helps to mitigate chain scission or crosslinking of polyethylene
- ENTEK will continue to work with customers to better understand how separators can be engineered to meet new battery life requirements in start-stop and other applications.