Techniques to Promote Oxidation Resistance in Polyethylene Battery Separators

Sunho Choi

Microporous LLC,
Piney Flats, Tennessee 37686 USA

Product Summary

Automotive				
Applications	**Battery Type**	**Legacy Products**	**New Products**	**Future Products**
SLI	SFB	DuroForce® Ultra™	CellForce® ULR™	
Start/Stop	EFB		CellForce® ULR™	
				DuroForce® OE
				DCA™ Booster Mat
				MaxiWik™
	AGM		GlassForce™	

Motive Power				
Applications	**Battery Type**	**Legacy Products**	**New Products**	**Future Products**
Forklifts	SFB	DuroForce® CL™		CellForce® XAS
				DCA™ Booster Mat
	AGM		GlassForce™	
LSEV	SFB	Flex-Sil®		CellForce® XAS
		CellForce®		
	AGM		GlassForce™	

Stationary				
Apllications	**Battery type**	**Legacy Products**	**New Products**	**Future Products**
Telecom/UPS	SFB	Ace-Sil®		
		DuroForce® CL™		
		CellForce®		
	AGM		GlassForce™	
ESS	AGM		GlassForce™	

Separators

- Legacy Products
- CellForce®ULR™
- GlassForce™
- DuroForce® OE
- CellForce® XAS™

Laminates

- DCA™ Booster Mat
- MaxiWik™

Pasting Papers

- GlassForce™

Technology Roadmap (2020-2025)

4Q19
GlassForce™

3Q20
CellForce® ULR™

3Q20
CellForce® XAS™

2021
DuroForce® OE™

2021
MaxiWik™

2021
DCA™ Booster Mat

2022-2025

Automotive:
- DCA, A/Ah: **2.0**
- PSoC, 17.5% DoD: **3,000**
- Water loss, g/Ah**: <3**

Motive Power:
- Faster Charging: **40A/100Ah**
- Longer cycle life: **at 80% DoD, Flooded: 2,500 cycles, VRLA: 1,500 cycles**

ESS
- PSoC life: **2,500 cycles**
- Deep-cycle life: **6,000**
- Charge efficiency: **>95%**

Telecom/UPS
- PSoC at 10% DoD: **>12,000**

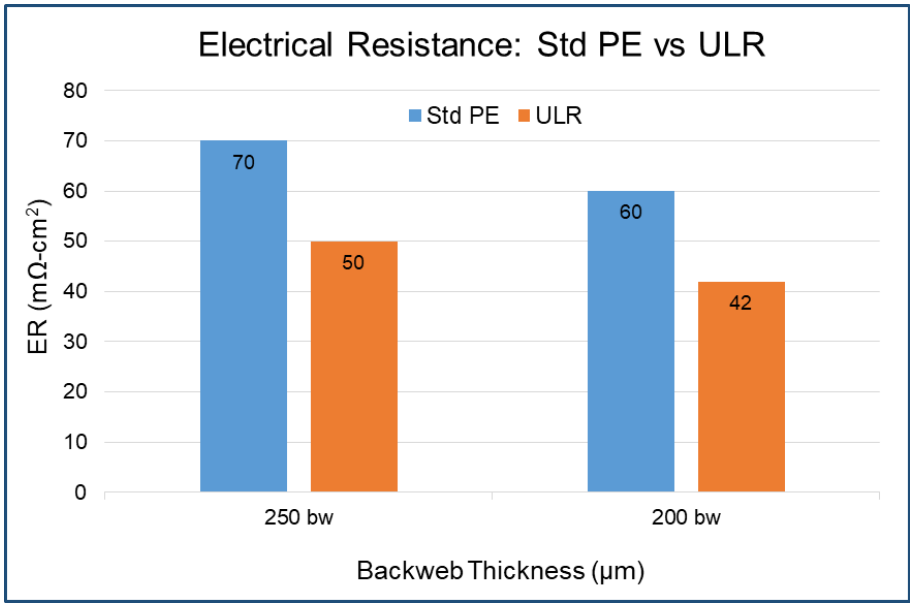
Source: Consortium for Battery Innovation (2020)

CellForce® ULR

Ultra Low Resistance Separator for Fast Charging in EFB, Golf Carts and Forklifts

30% Reduction in ER compared to Std PE separator

High Oxidation Stability through novel formula

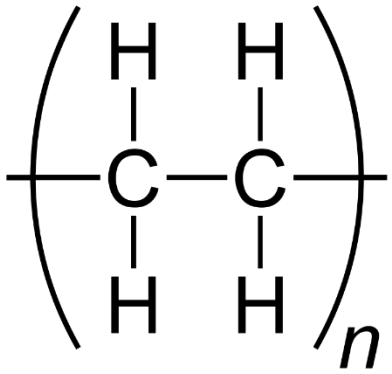


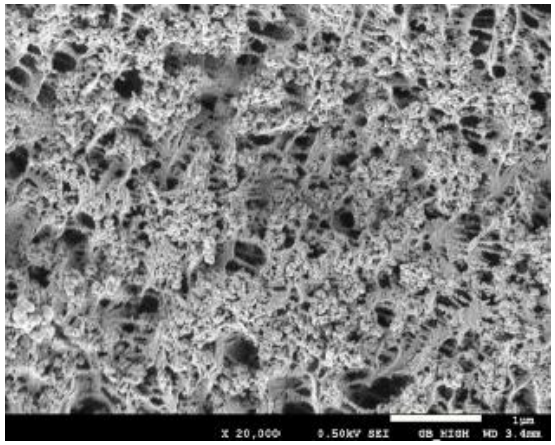
Challenge Identification

Goal: Develop the new separators with enhanced oxidation resistance

= Challenge: How can we reduce the chemical interaction of polymers?

→ How can we prevent the PE side groups from probable chemical interaction?





Probable Strategies

Technological Concept	Feasible Options	Pros	Cons
Reduce the number of side H groups	PE crosslinking (e.g., via catalysts or beam radiation)	• may offer better oxidation resistance	• possibility to change PE's mechanical properties • require additional post-production processes • not very cost-effective
Reduce the number of free radicals	Addition of radical trapping additives	• may not need additional post-production process	• need investigation of property changes • the additive functionality would be offset by other additives (e.g., wetting agent, etc.)
Making PE composites	Mixing of other polymers such as rubber	• may not need additional post-production process • proven data showing enhanced oxidation (e.g., with latex/rubber)	• max. achievable oxidation resistance would be lower than other options

Priority Determination

Decision factor: Time and Cost

Strategy #1	Strategy #2	Strategy #3	Strategy #4
PE composite	Additives	Crosslinking	New Polymer

Effect of Oil Types

Hypotheses: Effect of Aniline point to the oxidation resistance

- Aniline point (AP)
  - Definition: the lowest temperature at which an equal volume of aniline (C_6H_7N) is completely miscible with the tested sample
  - More aromatic compounds in the oil → more miscible with aniline → lower AP
    - or, High AP → higher alkane contents → lower amounts of aromatic and naphthenes
  - In technical oil, the aniline point is used to measure refinement levels
    - higher aniline point → higher level of refinement → higher oil stability
    - Aromatic content could directly affect oxidation if it's too high
      → Oils with less aromatic content would be better for less oxidation
      → **Oils with higher AP would be better for better oxidation resistance**

	A	B	C
Aniline point	87	85-93	94

- Assumption: **Oil C would show better oxidation resistance**

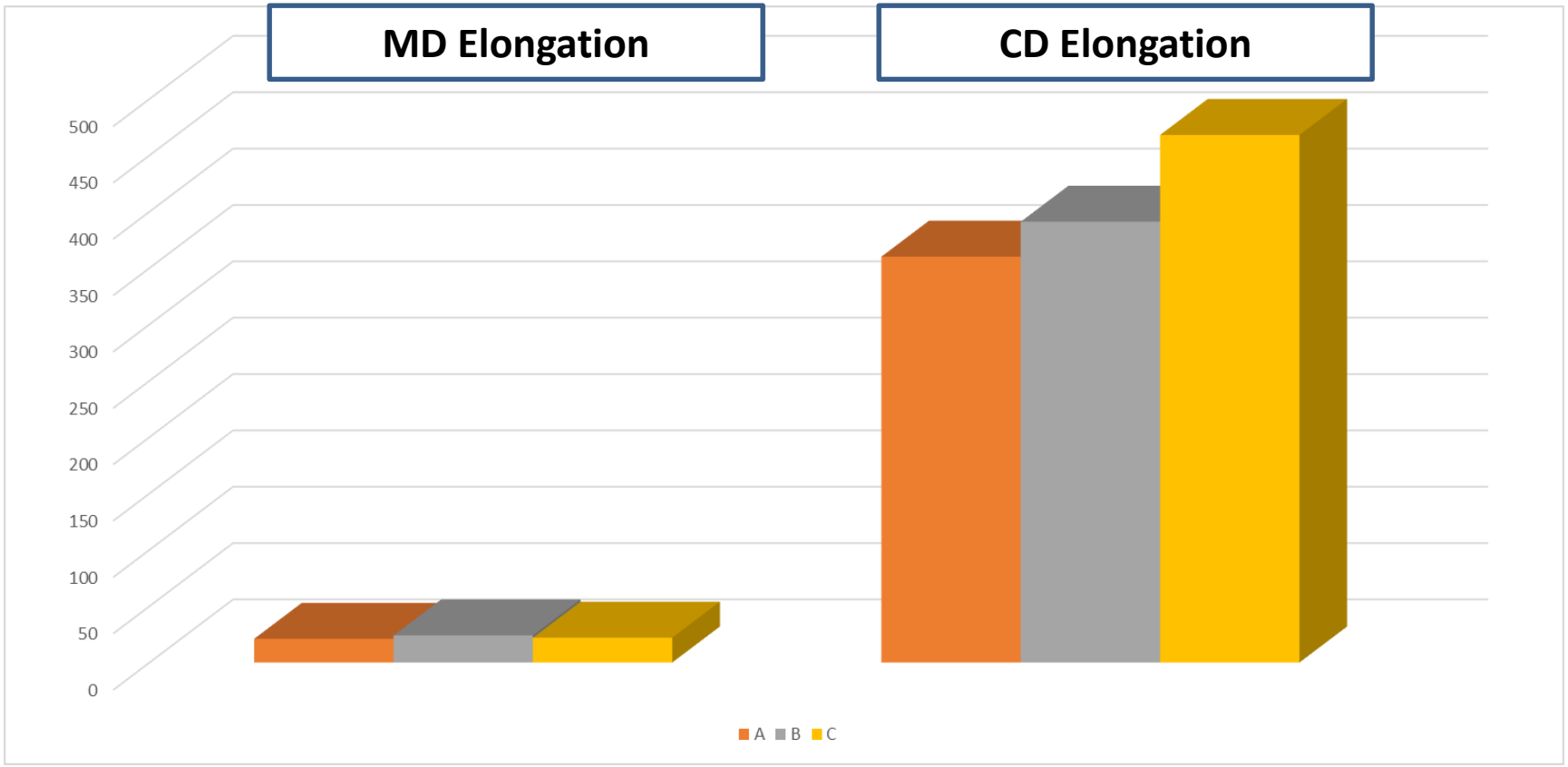
Effect of Oil Types

Sample Configuration

	A	B	C
Aniline point	87	85-93	94
Residual oil content (wt%)	17	17	18
Silica content (wt%)	28.6	28.6	28.6
Rubber content (wt%)	0.7	0.7	0.7
Backweb (in.)	0.011	0.010	0.010
Hg porosity (%)	64.2	62.8	63.2

Effect of Oil Types

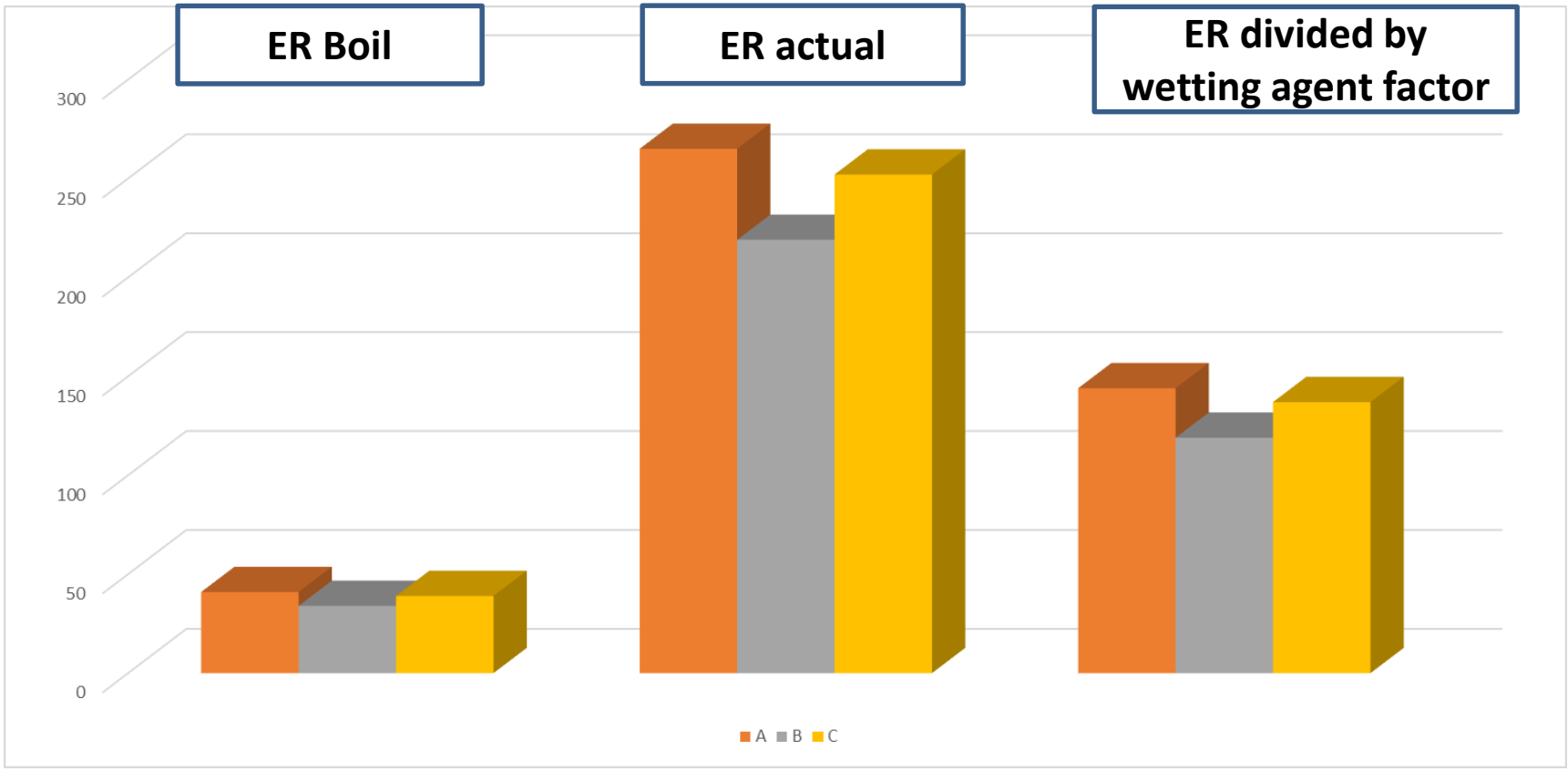
Results: Elongation



- MD Elongation: did not show significant differences
- **CD Elongation of Sample C: 20% ↑ (vs. B), 30% ↑ (vs. A)**

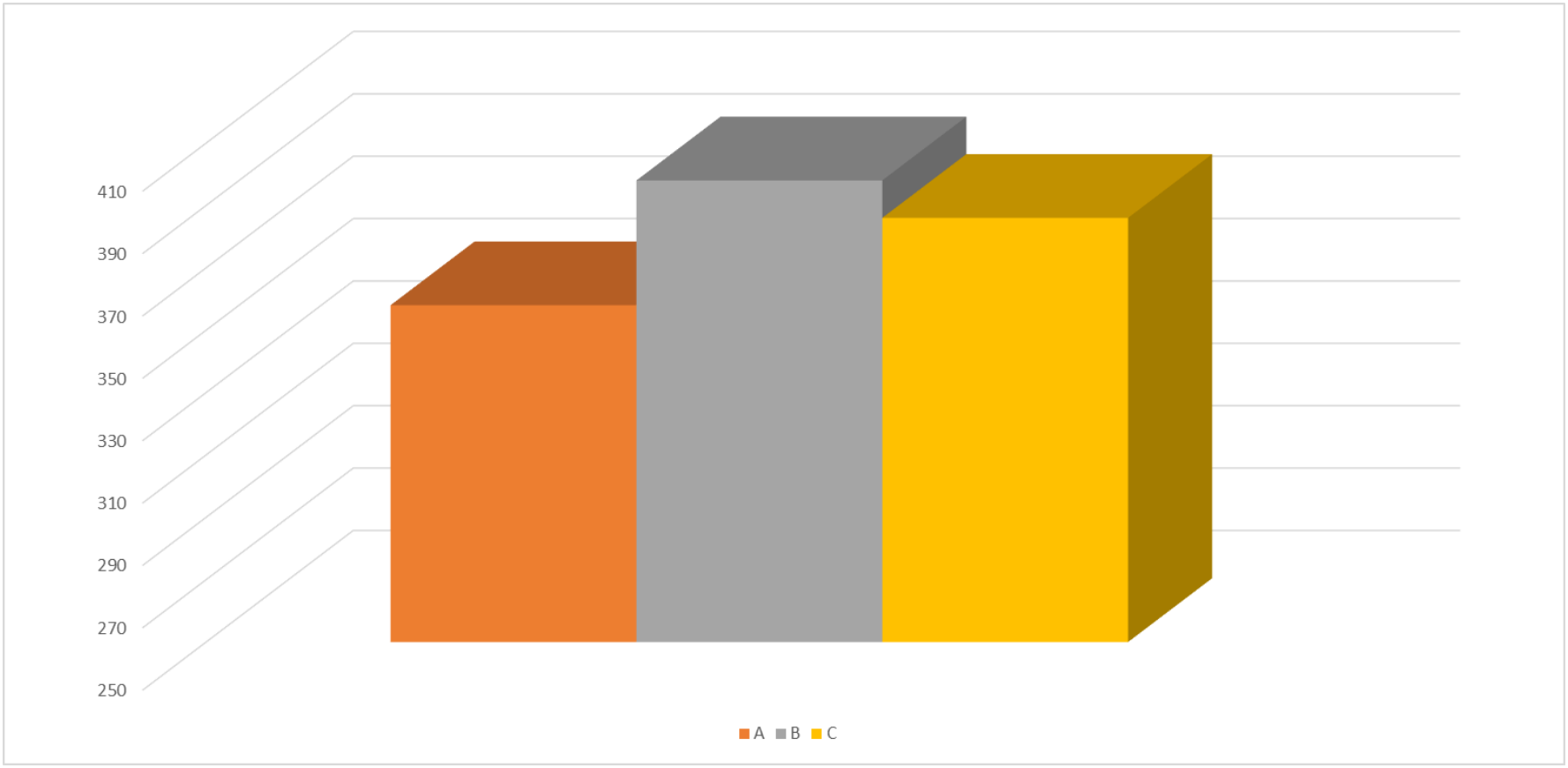
Effect of Oil Types

Results: ER



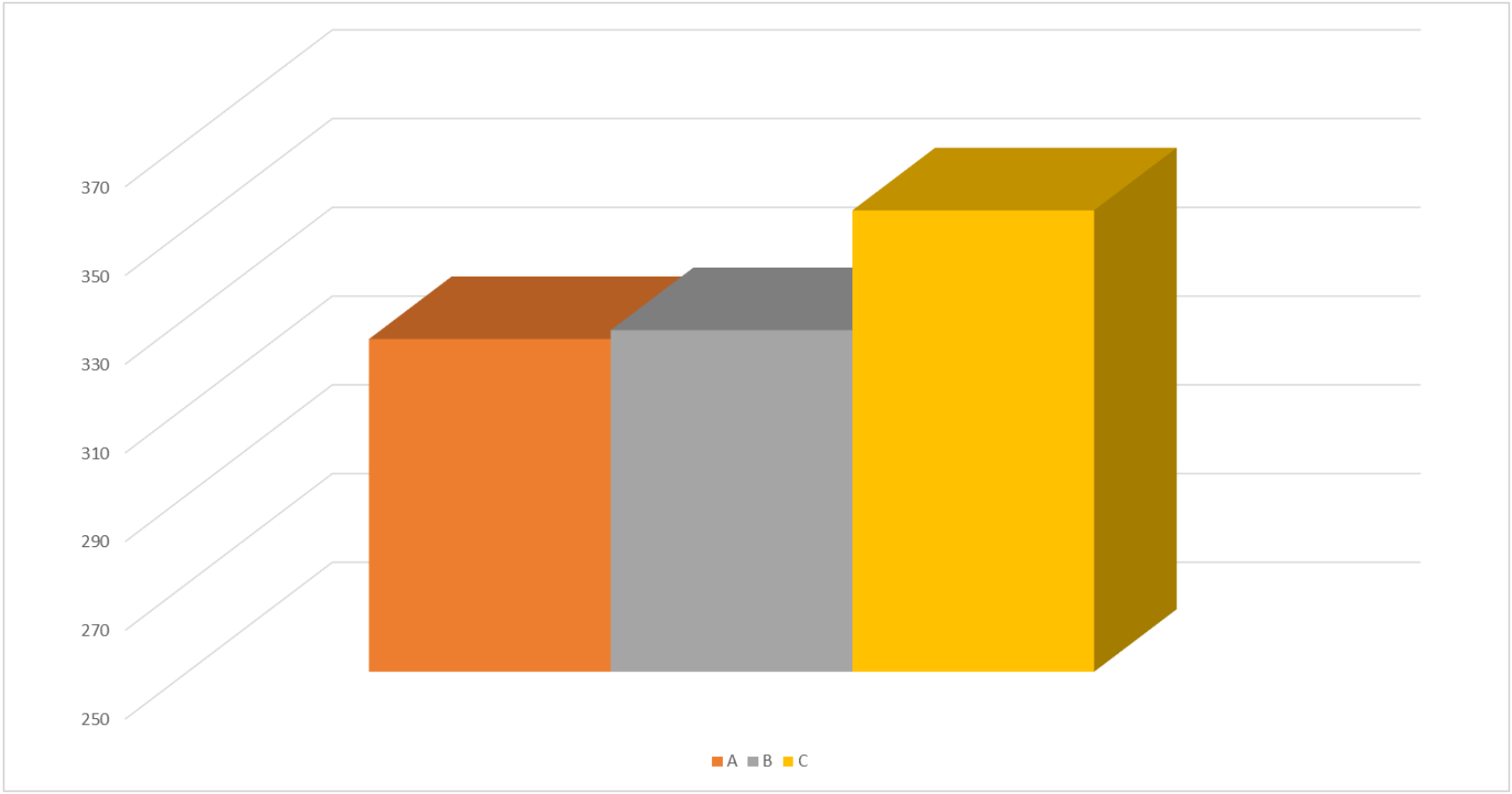
Effect of Oil Types

Results: Perox 40 Test



Effect of Oil Types

Results: Kill Test



- A and B do not show significant difference (less than 1%)
- **Kill test of C: 8.9% ↑ (vs. A), 8.3% ↑ (vs. A)**

Effect of Oil Types

Results: Summary

C	vs. A	vs. B
MD Elongation	-	-
CD Enlogation	30% ↑	20% ↑
ER	5% ↓	15% ↑
Kill test	**8.9% ↑**	**8.3% ↑**
Perox 40 test	7.8% ↑	3% ↓

- **High AP oil → Higher oxidation resistance especially at high temp conditions**

Effect of Rubber Amount

Hypotheses

- Patents by WR Grace and others
  - suggests that addition of latex/synthetic rubbers in PE can enhance oxidation stability

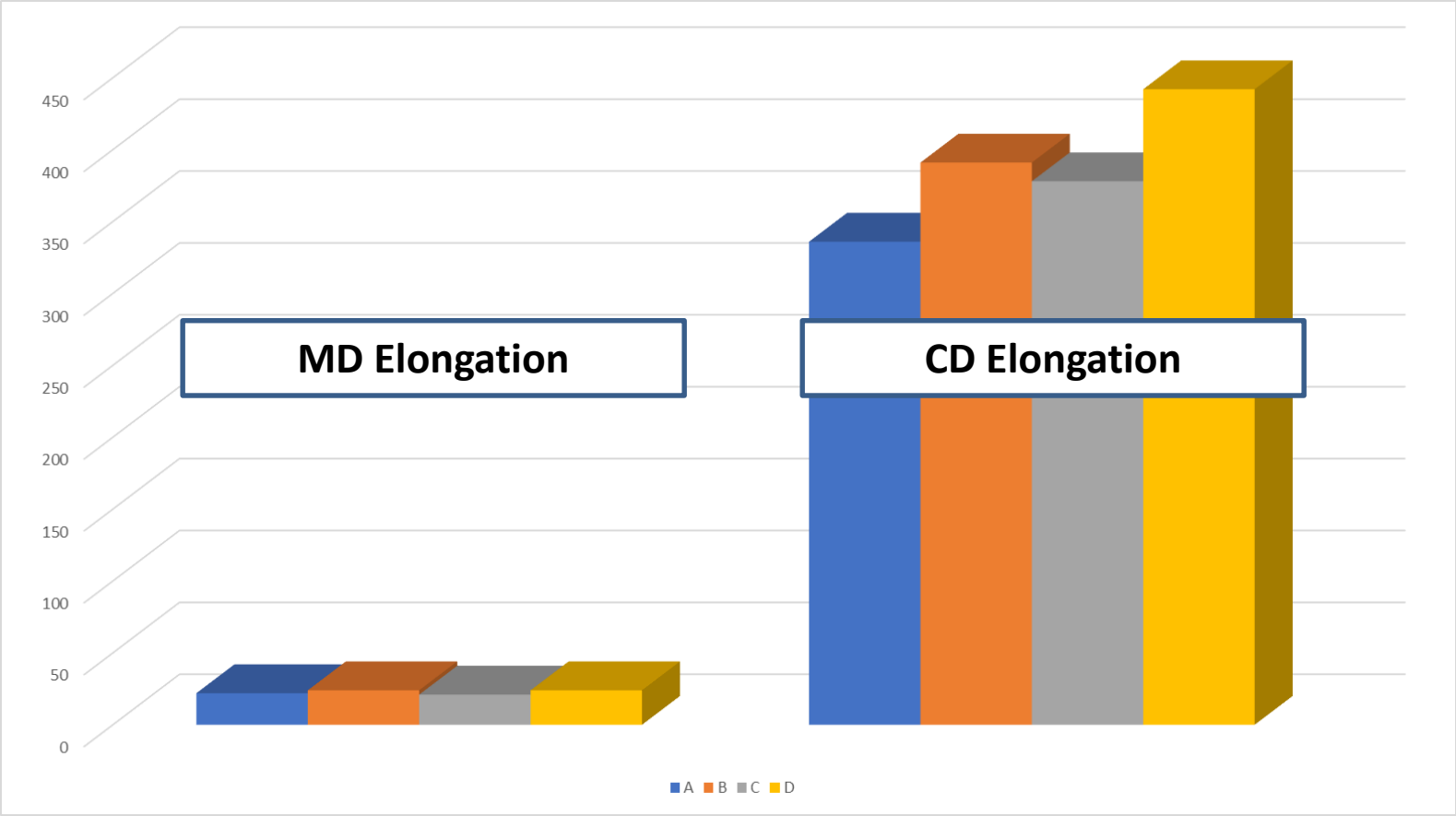
    → No clear mechanism or scientific explanation were provided

Sample Configuration

c	A	B	C	D
Rubber content(wt%)	**0**	**0.7**	**1.4**	**2.7**
Silica content (wt%)	28.6	28.6	28.6	28.6
Residual oil content (wt%)	16	17	17	17
Backweb (in.)	0.010	0.011	0.010	0.010
Hg porosity (%)	63.9	64.2	63.0	61.9

Effect of Rubber Amount

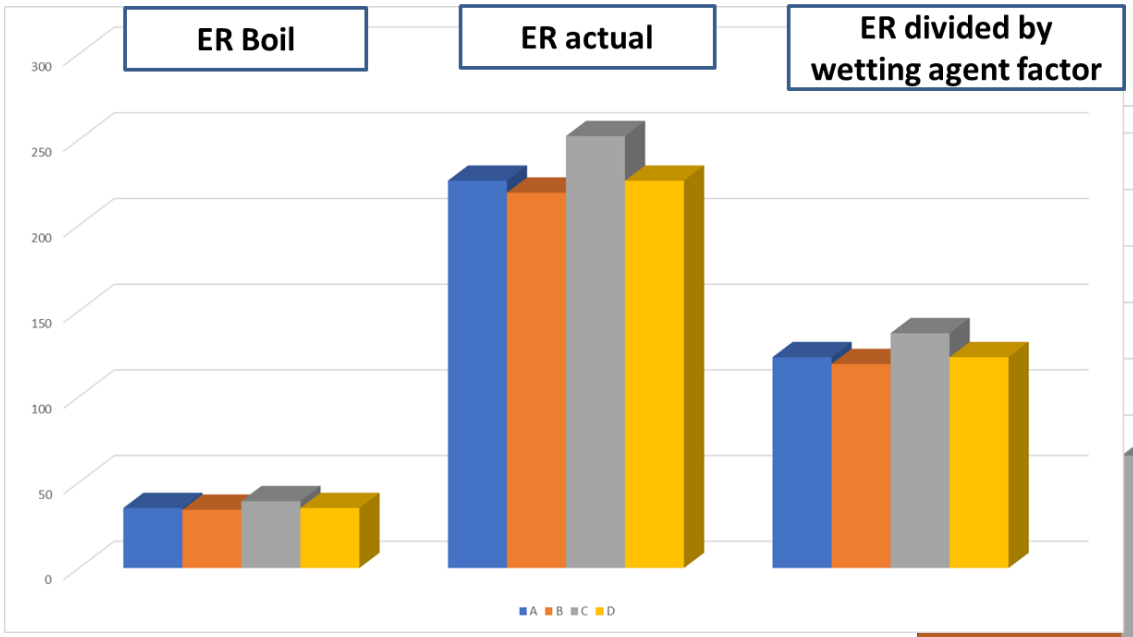
Results: Elongation

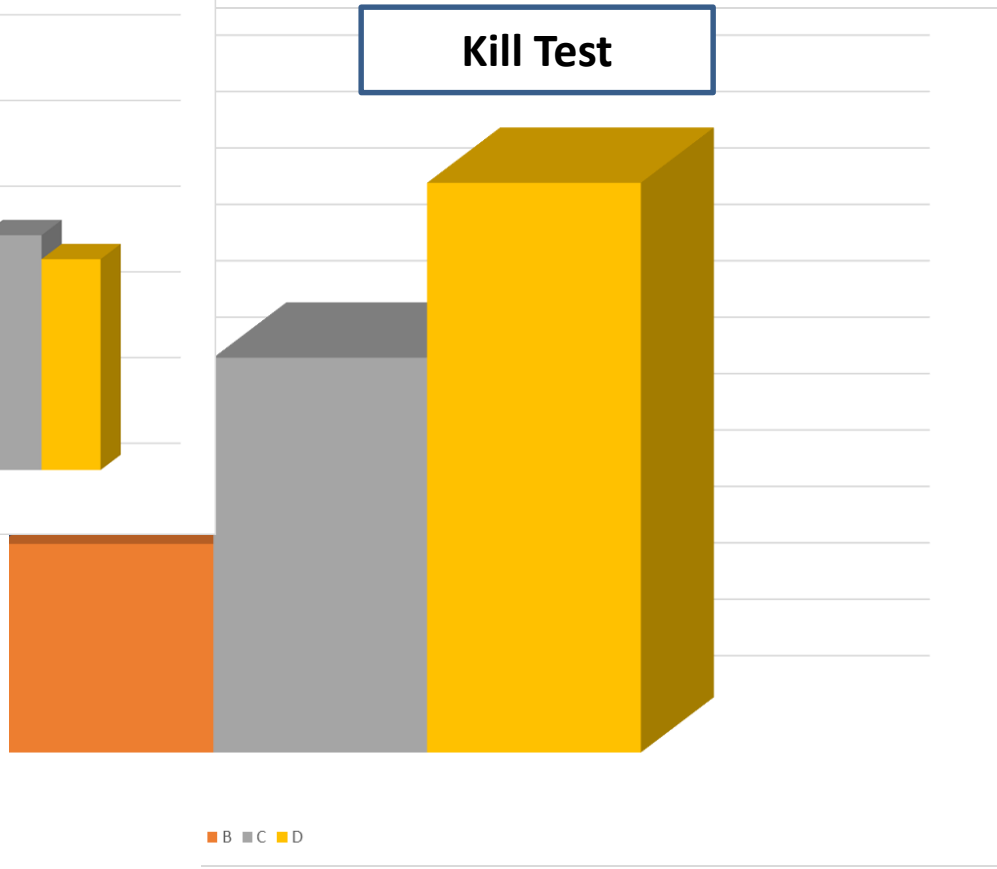


- MD Elongation: did not show significant differences
- **CD Elongation ∝ Rubber Amount**

Effect of Rubber Amount

Results: ER and Kill Test

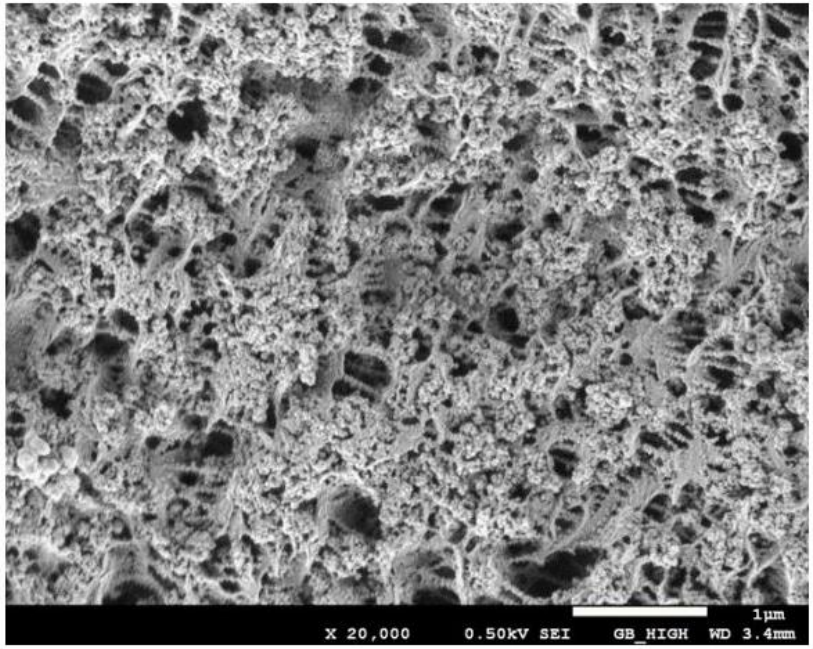




Effect of Rubber Amount

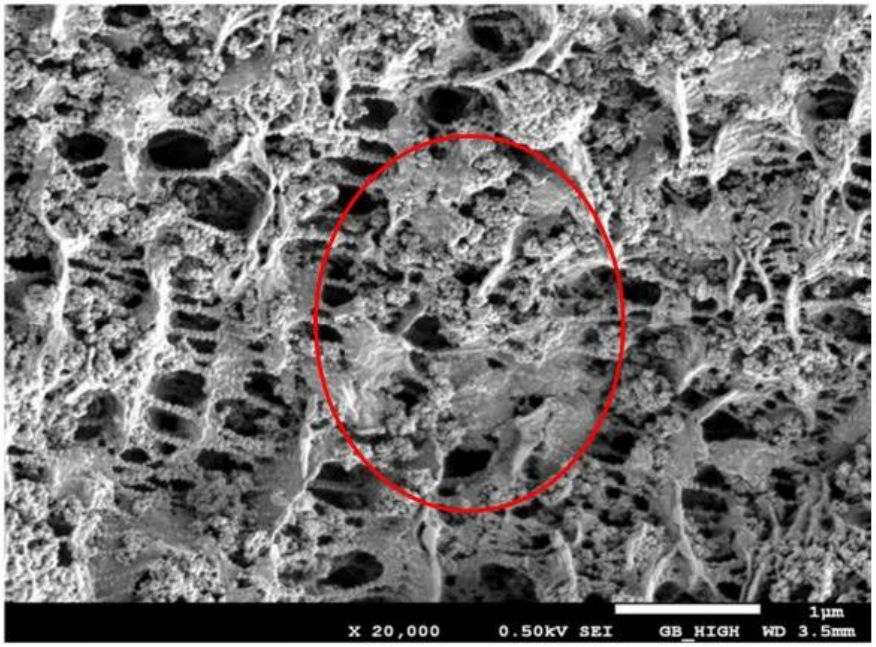
Hypothesis: Cross-linked rubber component?

SEM Micrograph 1.



20kX Micrograph of a typical PE separator (Microporous LLC)

SEM Micrograph 2



20kX Micrograph of a separator containing cross-linked rubber component

PE-Rubber Hybrid Separator (Microporous LLC)

Conclusion

- Microporous has been one of the most innovative battery separator companies
- Microporous has an extensive product lineup based on customer's needs, including the separators for automotive, motive power, and stationary
- Microporous recently launched a new product, CellForce® ULR, which shows
  - 30% reduction in ER compared to the standard PE separator
  - high oxidation stability through novel formula and processing
- CellForce ® ULR is an outcome of Microporous' continuous R&D effort through:
  - fundamental understanding of separator's structure-property-relationship
  - composite microstructures engineered to fine-tune the separator properties
- Microporous' research shows that the properties of oils and rubbers affect the separators' oxidation resistance significantly