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Powder Liquid Dispersions of Plasticizers to Increase Throughput and Meet Sustainability Goals for Tire Tread Formulations

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Agenda

- Background on tire compounding process
- Powder-Liquid Dispersions
- Goal of the Project
- Experimental Data & Discussion
- Conclusions
- Acknowledgements

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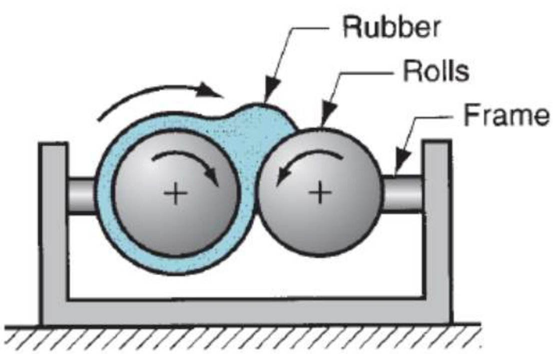
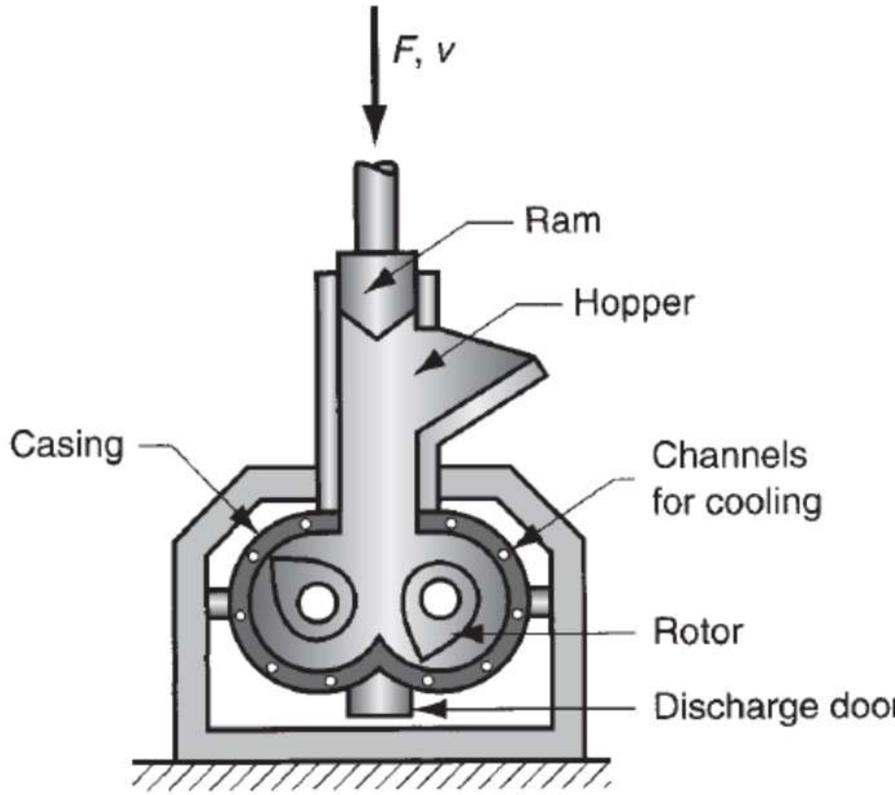
Background on Tire Compounding Process

- Steps in tire compounding process:
  - Breaking down elastomers via internal mixer compounding (peptizers)
  - Addition of plasticizers, CB or silica and process aids
  - Addition of the balance of fillers and AOs
  - Addition of vulcanization components
- Rubber mixing process occurs at high temperatures up to 180°C

Background on Tire Compounding Process

- Overtime, process shifted away from "***open-mill processing***" toward "***internal mixer compounding***"
- Compounding is purposely designed to yield uniform dispersion of all compounding materials in a tire tread formulation
- Shift to internal compounding processes led to increased automation, efficiency, quality, compound uniformity and cost savings





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Background on Tire Compounding Process

- Detailed design of mixing cycles and order of addition of raw materials are typically governed by a set of well-known guiding principles:
  - Separate high-tack resins from dry powders
  - Hold the batch drop temperature above the Tg of the hard resin component
  - Contain liquids to prevent leakage and raw material losses
  - Make use of the shear properties of rubber to accelerate mixing, and
  - Avoid scorch and subsequent formation of cured/crosslinked particles and crumb
- Some of the principles had been further addressed by the incorporation of dry powder-liquid dispersions (PLD), such as SUPRMIX®

Powder-Liquid Dispersions (PLD)

- PLDs are powder products made by dispersing liquids onto a dry powder carrier such as, amorphous silica, Ca-silicate or others
- PLDs are:
  - Low dust
  - Free-flowing powder mixtures
  - Contain about 50-80 wt% of liquid active materials
  - *SUPRMIX® typically contain 72 weight % of active liquid material*
- Typical actives include plasticizers, coumarone-indene resin, epoxy resins, waxes, petrolatum, liquid polymers, anti-oxidants, peptizers, co-agents, process oils, adhesion promoters and more

Benefits of using PLDs in Rubber Compounds

- Improved handling
- Improved batch-to-batch consistency
- Reduced employee exposure (with hazardous actives)
- Reduced spill potential
- Improved batch incorporation and compound consistency
- Reduce equipment clean out
- Reduced residual chemical disposal
- Reduced drum disposal
- Also available in low melt pre-weighs for easier handling and more accurate charging

Goal of the Project

- To determine mixing time, torque, and energy consumption to emphasize the efficiency and sustainability gains realized from incorporation of PLDs
- To use tire tread formulations to confirm that physical data are not affected by a shift from liquid plasticizers to powder liquid dispersions

Experimental Data & Discussion

Rheomix 600 parameters (77 rpm, 93ºC)	DOP	SUPRMIX® DOP
Plasticizer level (phr)	30	30
Maximum torque (m.kg)	2.08	2.40
Compound temperature (ºC)	108	111
Maximum energy (kJ)	64	46
Dispersion time (min)	10.0	7.0

- Collaborative study with a major compounder in a proprietary NBR formula
- Observed 30% improvement in cycle time by utilizing Suprmix® PLD
- About 28% reduction in energy requirement for the compounding process
- In an actual plant run, mixing time was reduced from 210s to 90s

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Experimental Data & Discussion

DOTP formulations (parts)	Formula #1 (DOTP)	Formula #2 (SUPRMIX® DOTP)
NBR	100	100
Carbon Black	75	75
Hard Clay	80	80
Silica	11.6	
DOTP	30.0	
SUPRMIX® DOP		41.6
TOTAL	296.6	296.6

- Comparative study was done in compositionally identical NBR formulations
- Testing was conducted in triplicates and results averaged
- The rotor speed of the mixer remained constant throughout the compounding of all 6 batches

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Experimental Data & Discussion

DOTP formula	Mix time	kWh
#1 - Liquid	291.3	35.3
#2 - SUPRMIX®	280.0	33.8
Δ	11.3	1.5
Δ%	3.9%	4.2%

- Mixing of each batch was stopped once the target temperature of a compound was achieved
- Results indicate an average mix cycle time reduction of 3.9% and power reduction of 4.2% when PLD version of the plasticizer is employed

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Experimental Data & Discussion

DBEEA formulations (parts)	Formula #3 (DBEEA)	Formula #4 (SUPRMIX® DBEEA)
NBR/PVC (70/30) blend	142.8	142.8
Carbon Black	35.0	35.0
Hard Clay	85.0	85.0
Silica	21.8	
DBEEA	56.0	
SUPRMIX® DBEEA		77.8
TOTAL	340.6	340.6

- This comparative study was done in compositionally identical NBR/PVC blend formulation using the same test protocol

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Experimental Data & Discussion

DOTP formula	Mix time	kWh
#3 - Liquid	323.7	17.2
#4 - SUPRMIX®	236.3	14.4
Δ	87.3	2.8
Δ%	27.0%	16.2%

- Results of this test study show 27% improvement in the mix cycle time and 16.2 % reduction in the energy consumption during mixing process

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StarTread® Selection

	Highlighted performance advantages in tire-tread compounds		
Ester Product	**Winter**	**Wet**	**Roll**
StarTread® A-140	Good	**Excellent**	**Excellent**
StarTread® A-200	Good	Good	Good
StarTread® A-400	**Excellent**	Poor	Good
StarTread® A-700	Good	**Excellent**	Good
StarTread® A-900	Poor	**Excellent**	Poor

- The 2nd goal of the project was to demonstrate similar performance between formulations made with liquid plasticizers and PLDs
- Performance advantages of selected StarTread® products are based on DMA data parameters widely used in the tire industry

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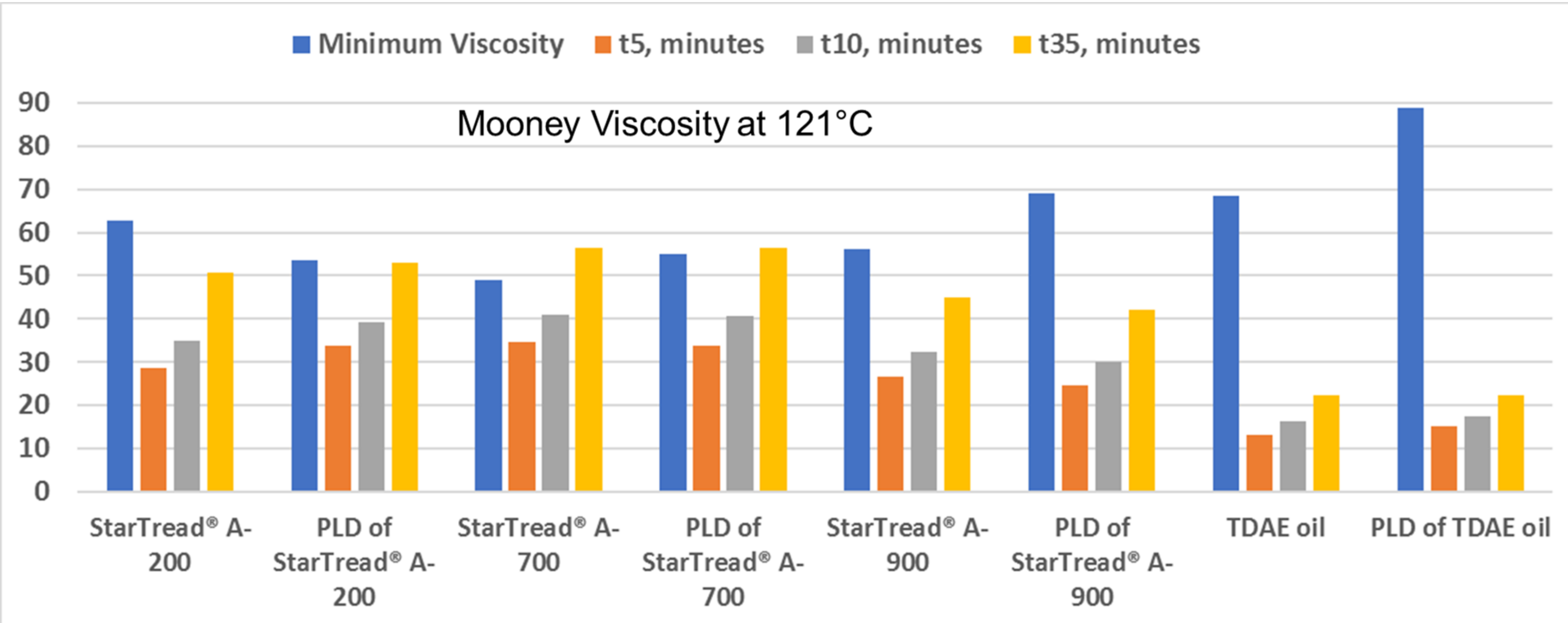
StarTread® liquid and PLD tire compound formulations

Material	StarTread® A-200	StarTread® A-400	StarTread® A-700	StarTread® A-900	TDAE oil	PLD of StarTread® A-200	PLD of StarTread® A-400	PLD of StarTread® A-700	PLD of StarTread® A-900	PLD of TDAE oil
	Parts (phr, wt.)									
Duradene 739 S-SBR	75.00	→								
Diene 645 BR	25.00	→								
Hi-Sil 190G (silica)	80.00	→								
X 50-S (reinforcing agent)	12.80	→								
Norman-346 (TDAE oil)	16.25	→								
Kadox 920 (zinc oxide)	2.5	→								
Staric acid	1.00	→								
Antiozonant Vulkanox 4020 (6PPD)	2.00	→								
Nochek 4729 (paraffin wax)	1.50	→								
StarTread® A-200	16.25	-				22.57				
StarTread® A-400		16.25					22.57			
StarTread® A-700			16.25					22.57		
StarTread® A-900				16.25					22.57	
TDAE oil					16.25					22.57
Subtotal	**232.30**	**232.30**	**232.30**	**232.30**	**232.30**	**238.62**	**238.62**	**238.62**	**238.62**	**238.62**
Mill Addition										
Sulfur	1.40	→								
Vulkacit CZ (sulfonamide)	1.70	→								
Akrochem Accelerator DPG (diphenylguanidine)	2.00	→								
Total	**237.40**	**237.40**	**237.40**	**237.40**	**237.40**	**243.72**	**243.72**	**243.72**	**243.72**	**243.72**

Comparative Mooney Viscosity Data



Liquid and PLD compound samples exhibited similar performance characteristics

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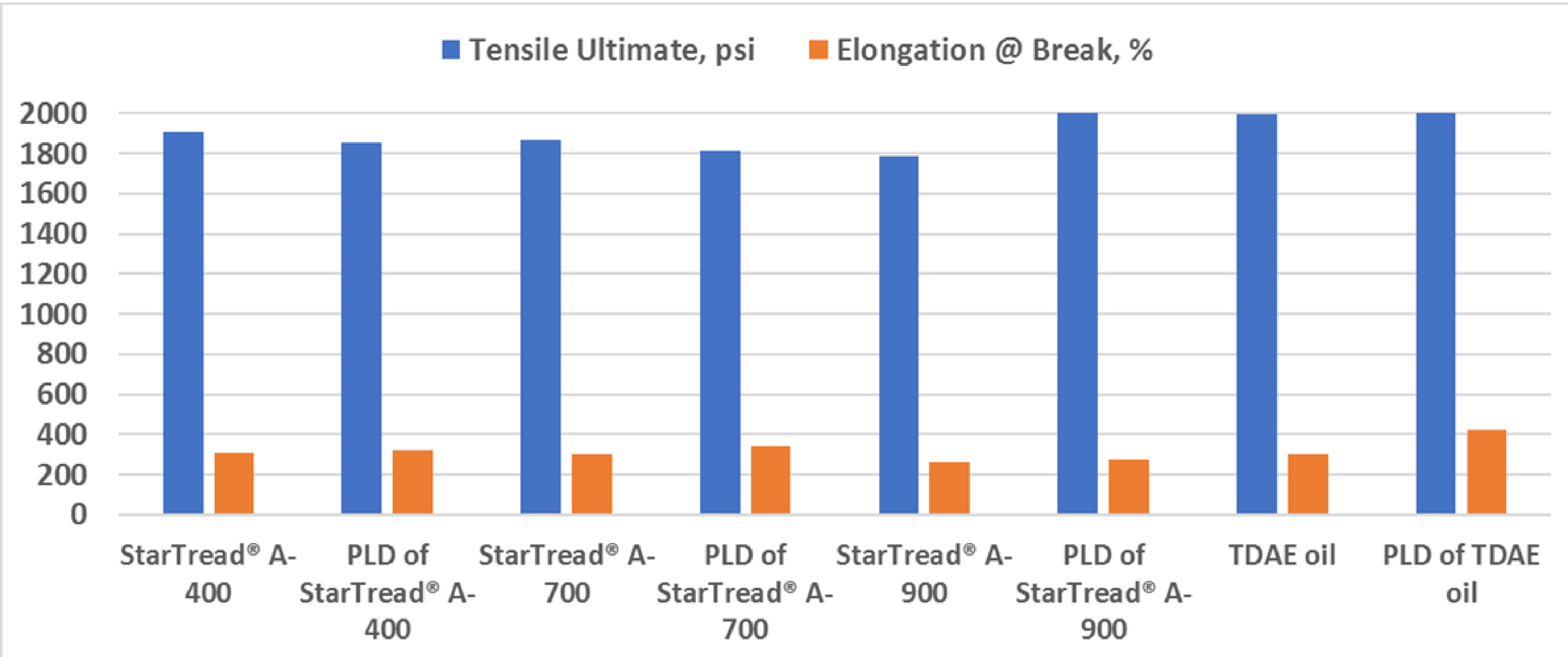
Original Mechanical Properties



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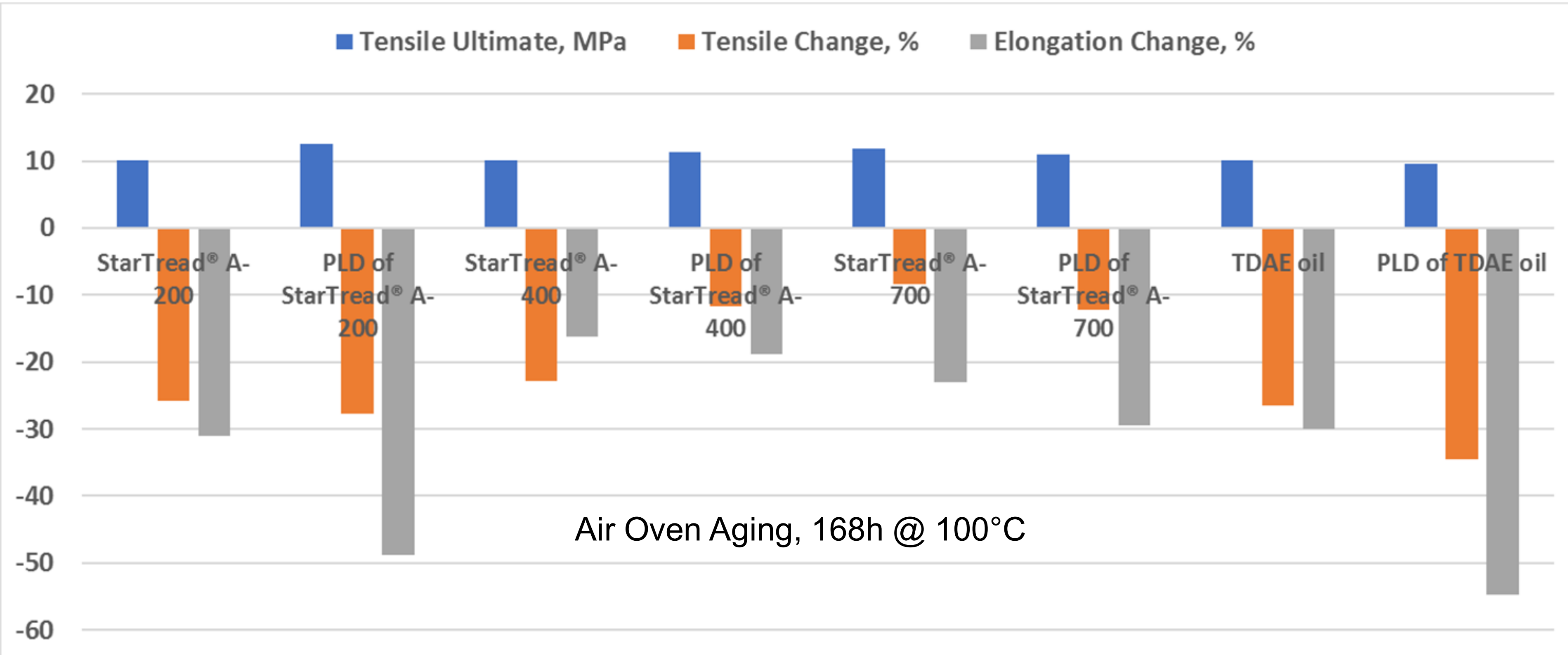
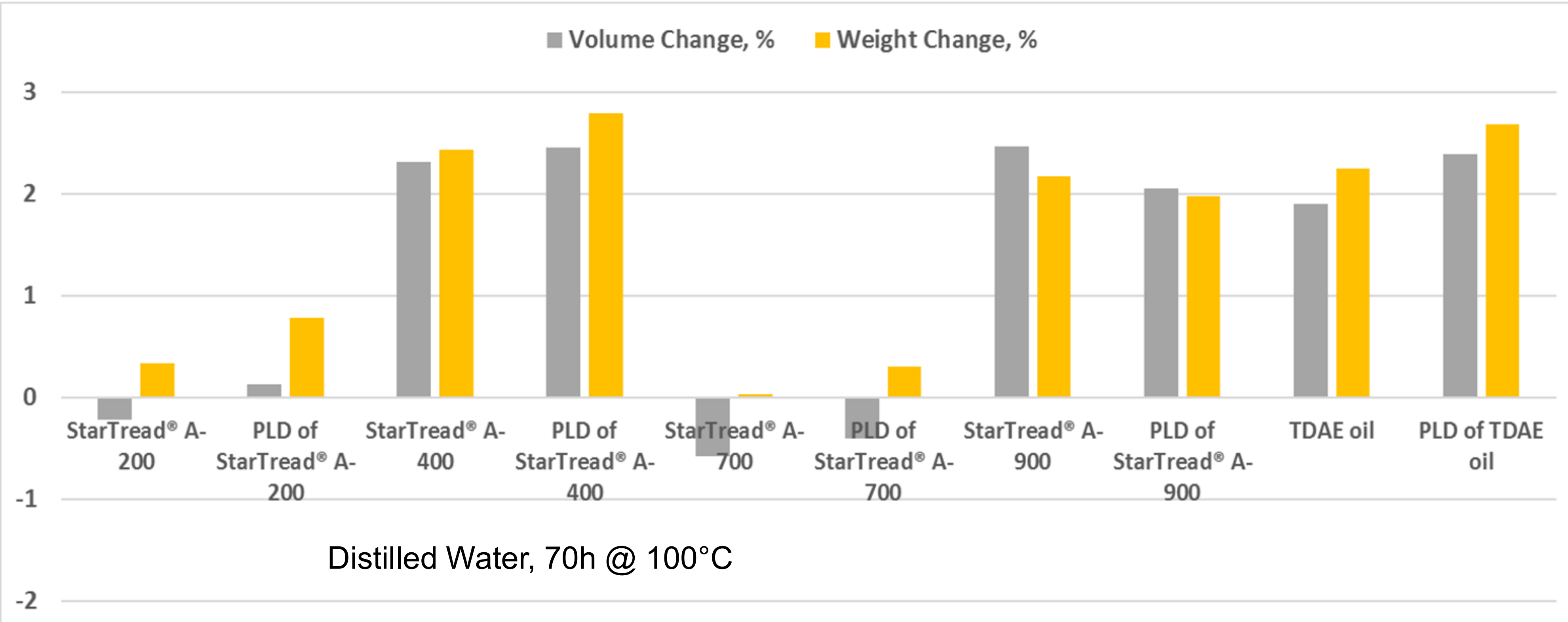
Aged Mechanical Properties



Fluid Resistance Properties



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Conclusions

- PLD versions of liquid rubber additives show significant improvement in mix cycle times and in total power consumption.
- Positive impacts on the cycle time and energy consumption are demonstrated
- PLDs also have significant positive impact on the environment
- U. S. Department of Energy estimates that coal power plants generate approximately 2.1 lbs of carbon dioxide (CO_2) per kilowatt hour (kWh) of electricity produced.
- Estimating a reduction of 2.15 kWh per batch based on the mix data presented above, a rubber mixing facility that produces 40,000 batches per year would save 86,000 kWh's.
- This would further translate to a reduction of approximately 180,600 lbs of CO_2
- Results for each pair of liquid StarTread® and PLD formulations exhibit small performance differences which indicate that end-users could easily replace liquid additives in their tire formulation with their PLD analogues without a fear of drastic performance changes.

Acknowledgements

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