The Use of Soy-based Oils to Incorporate Recycled Crumb Rubber into Automotive Rubber Composites

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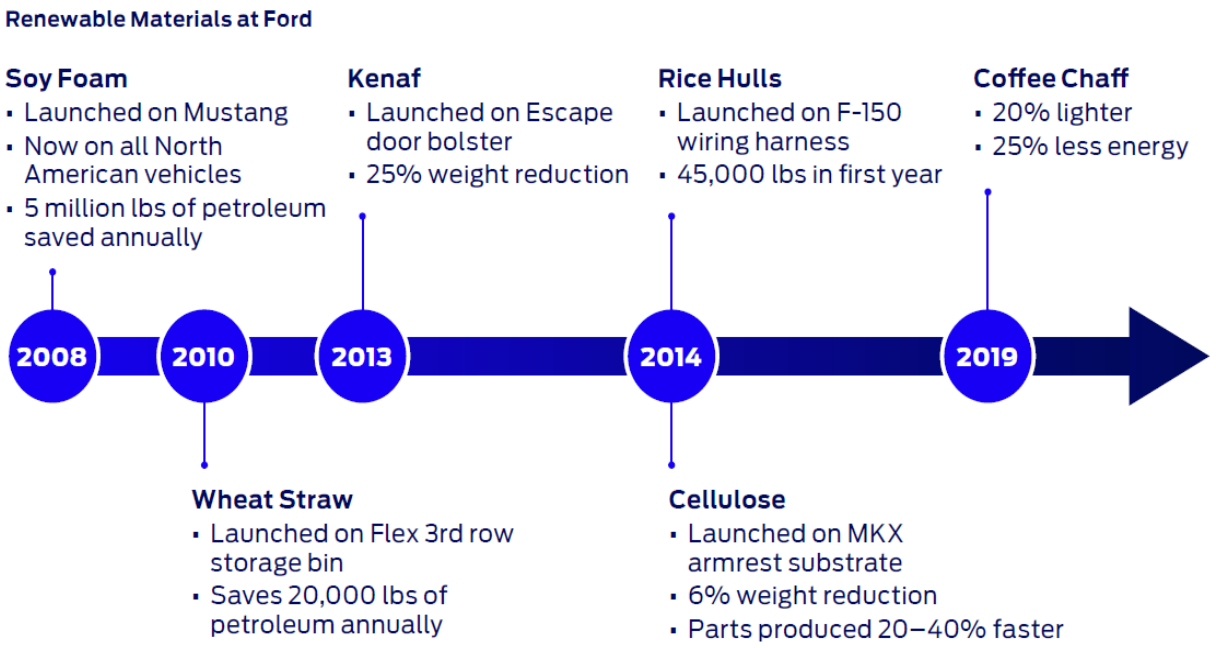
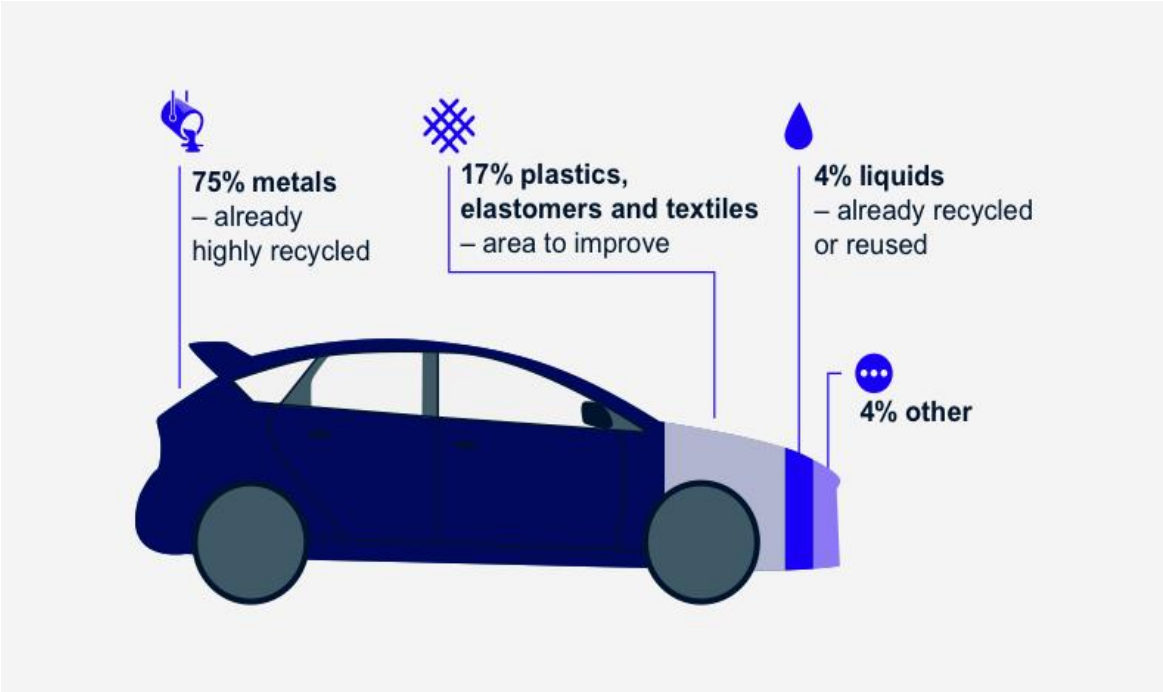
Ford and Sustainability





*From Ford 2021 Integrated Sustainability and Financial Report

Ford Goal: To utilize only recycled or renewable content in vehicle plastics

Project Goals

- Use soy-derived oils for pre-processing and de-vulcanization of micronized recycled rubber (MRP) for the use as a cost-effective filler in rubber compounds for automotive floor mats
- Maximize MRP content in rubber formulations while maintaining performance properties
- Elimination of petroleum-based processing oil used in styrene-butadiene rubber (SBR) compounds
- Optimize formulation for automotive floor mat applications

Tire Disposal

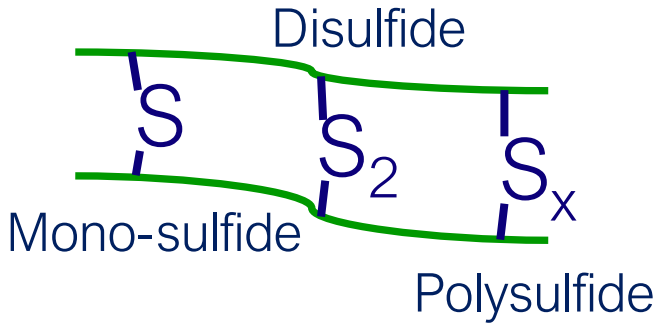
- U.S. disposes of about 300 million tires each year
- Approximate annual US vehicle production at Ford – 2.6 million vehicles = 10.4 million tires
- Tires (~14 lbs x 4/vehicle)

Tires End-of-Life

- **Material recovery**; ground rubber used in pavement bases, artificial turf for sport fields
- **Energy valorization**; tire-derived fuel to power furnaces in cement plants and paper mills
- These disposal methods affect water and air quality
- Tire recovery rate ~80-90%, there are still millions of tires landfilled or illegally discarded.

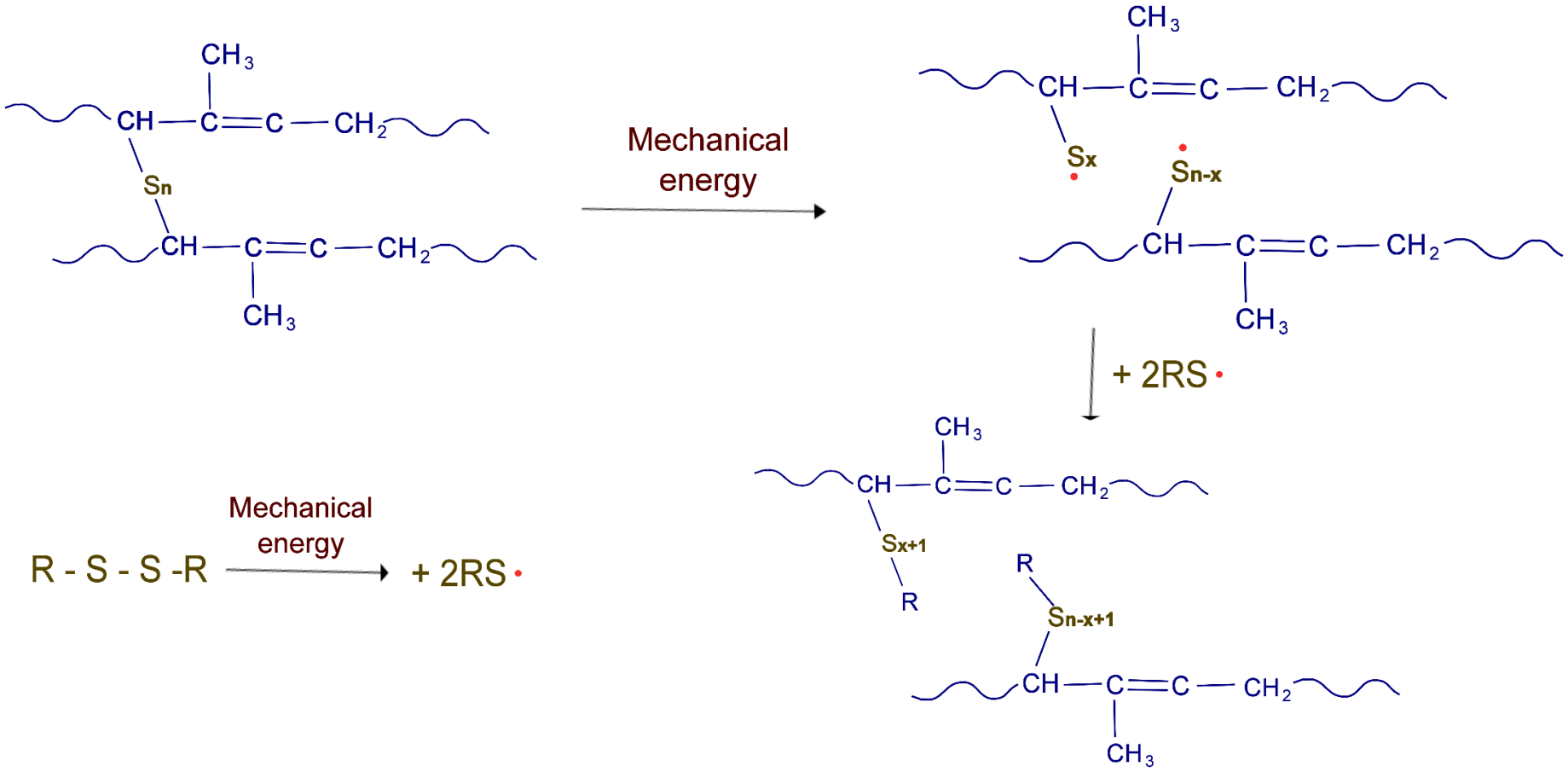
How do we get recycled crumb rubber?

- Process used tires in order to produce micronized rubber powder (MRP)
  - Creates a powder from a stable 3-D network of vulcanized rubber
  - Network based on sulfide linkages
- Benefits of using MRP in rubber production
  - Cost reduction for end products
  - Increase sustainability of material
- MRP must be partially devulcanized before use in automotive applications
  - Physical properties of rubber compound will deteriorate if vulcanized MRP is added into the compound
  - Partial devulcanization to prevent degradation of polymer



Bond	Dissociation energy, kJ/mol
S-S	251
S-C	272
C-C	346

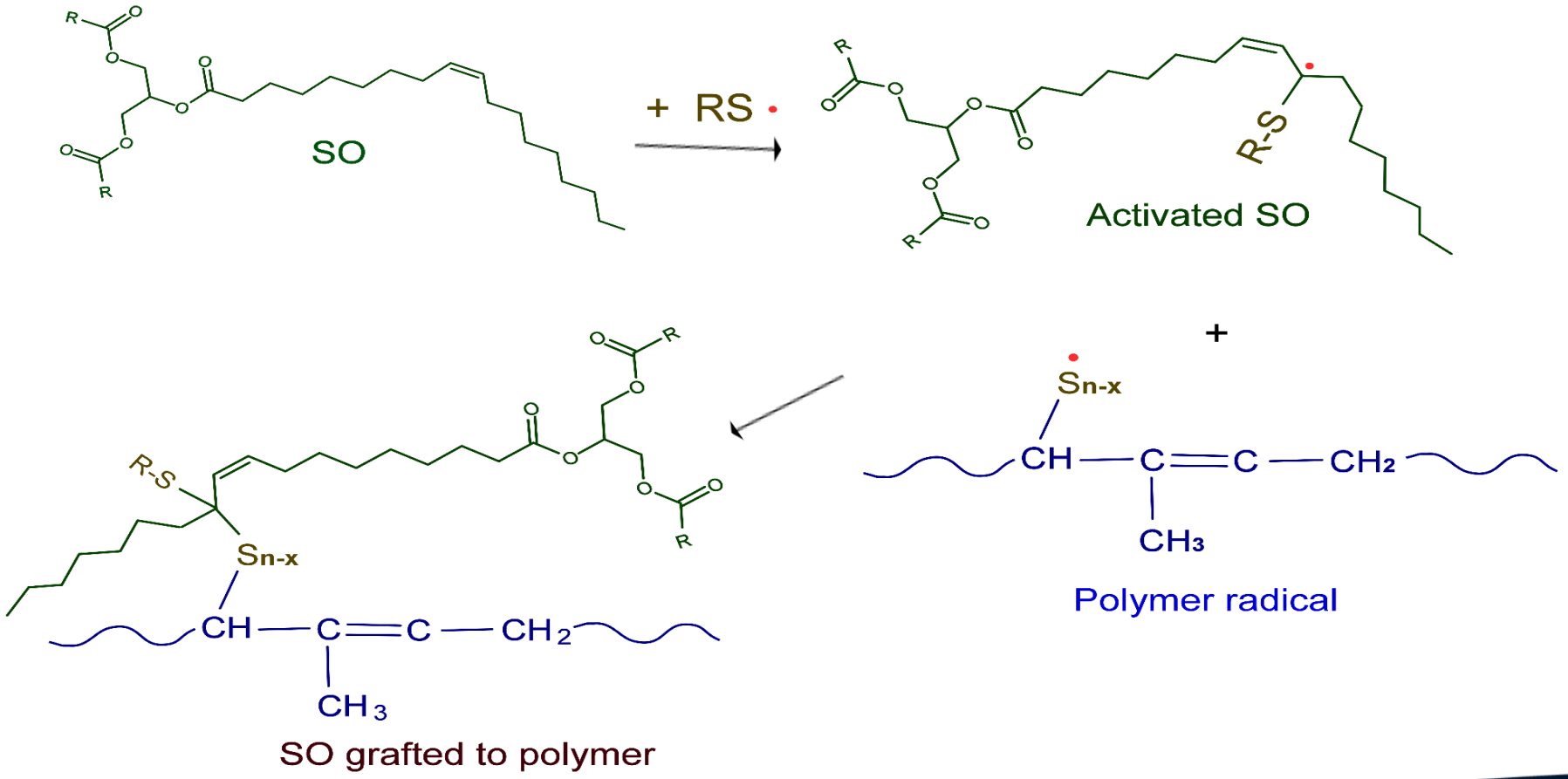
What is mechano-chemical devulcanization process?



D. De, S. Maiti, and B. Adhikari. J. Appl. Polym. Sci. 73, 2951, (1999).

How can we use soybean-based oils to devulcanize MRP?

In presence of soybean oil (SO)



Our MRP pretreatment: mixing 60 phr of MRP with 30 phr of oil, 45/60 phr of carbon black, and 1 phr of TMTD for 15 min

What is needed to make an SBR compound?

Base Polymer Material

Ability to deform and recover

Vulcanizing Agent (Sulfur)

Cross-links rubber to improve properties (stiffness) and widen use temperature range

Processing Oil

- Improves ability to process compound during manufacturing
- Controls hardness

Fillers (Carbon Black)

- Mechanically reinforce rubber
- Improves wear and physical properties

Other Chemicals

- Antioxidants and antiozonants are added to provide thermal stability and durability with peroxide-cure
- Accelerators are added to control the cross-linking reaction with sulfur-cure
- Processing aids are used to improve the mixing process

Formulation of SBR Compounds in the Lab

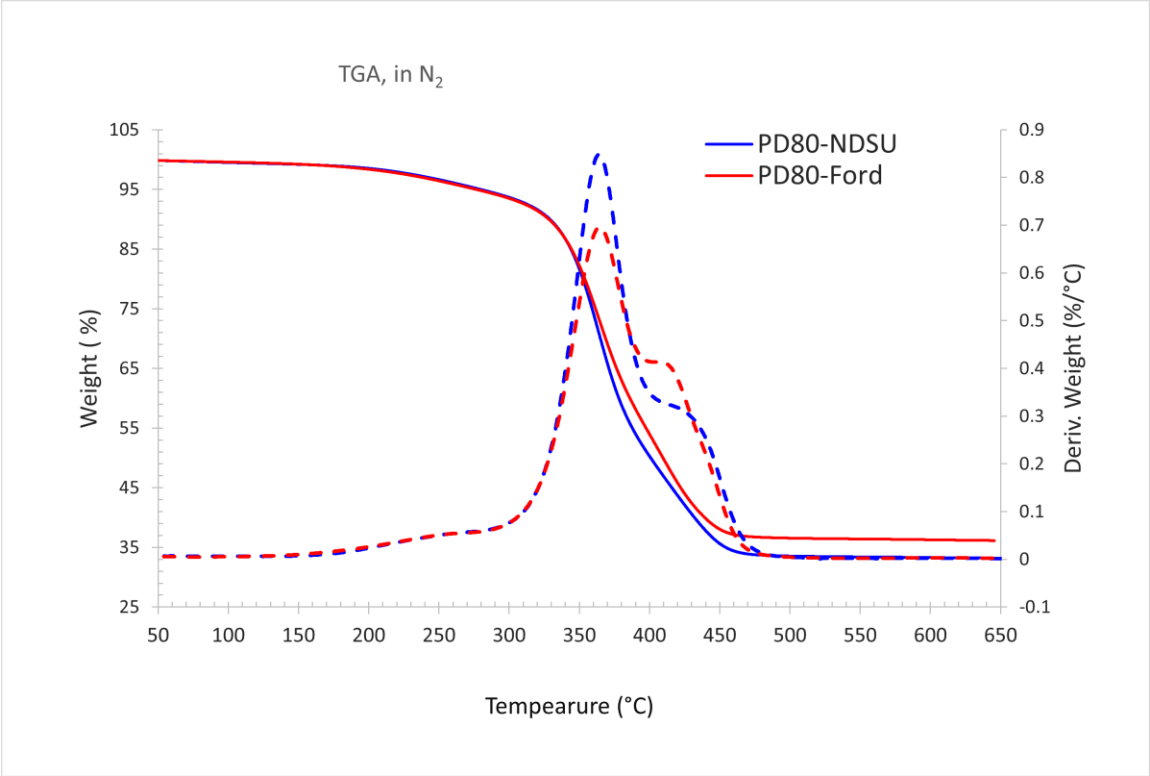
- Rubber formulations are measured in parts per hundred rubber (PHR)
- In the formulation of interest, the amount of processing oil used is 30 PHR
  - 6.9% by weight of total compound
- The following oils were tested
  - Naphthenic
  - High oleic soybean oil (HOSO)
  - Soybean oil (SBO)
  - Functionalized soybean oil (SBO-PS20)
- The following types of recycled tire rubber were tested
  - PD-80-TR
  - PD-140-TR

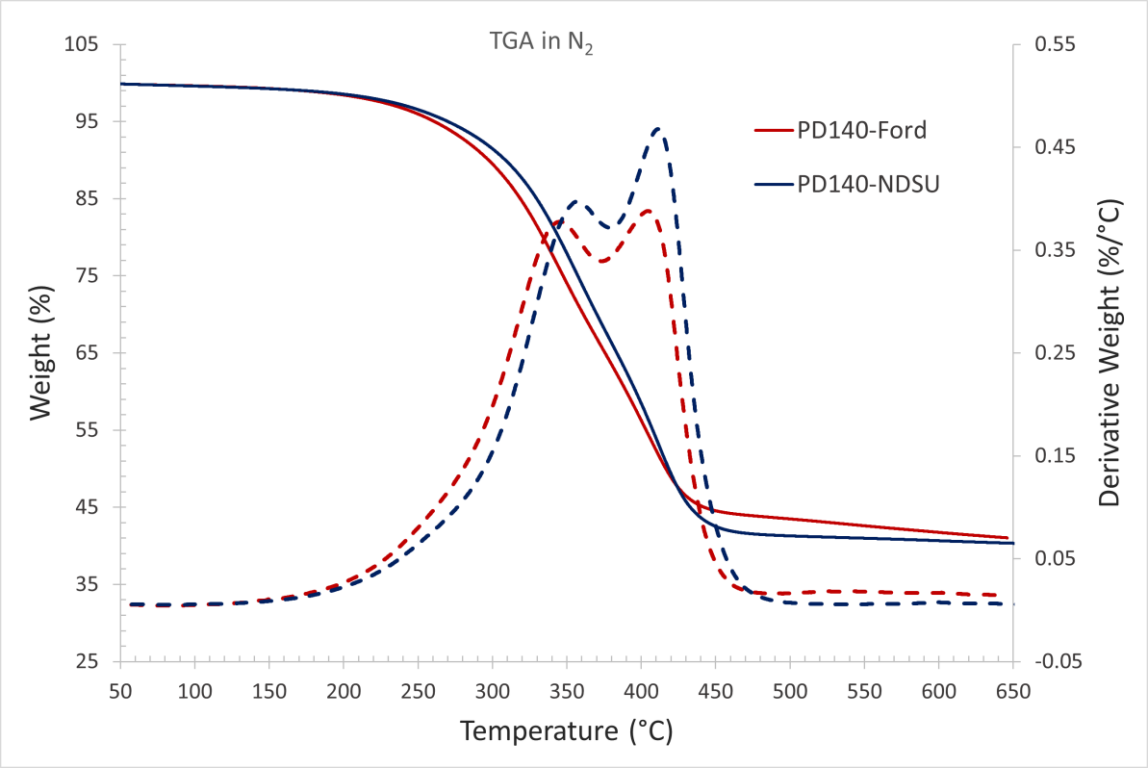
Purpose	Ingredient name	PHR
Rubber Base Material	SBR Rubber	60.00
MRP	PD-140-TR	60.00
Plasticizer	High Oleic Soybean Oil	30.00
Reinforcing Filler	N550 Carbon Black	45.00
Devulcanizing Aid	TMTD	1.00
Vulcanization Activators	Zinc Oxide	5.00
	Stearic Acid	1.00
Vulcanization Accelerators	Naugex MBTSW (MBTS)	0.50
Antioxidant	DQ	1.00
Vulcanizing Agent	Sulfur	2.20
	Total	205.70

Evaluation of SBR Compounds in the Lab

- Thermal Analysis of MRP (TGA)
- Rheometry
- Tensile/Hardness Properties
- Tear Strength

Thermal Analysis of MRP (TGA)

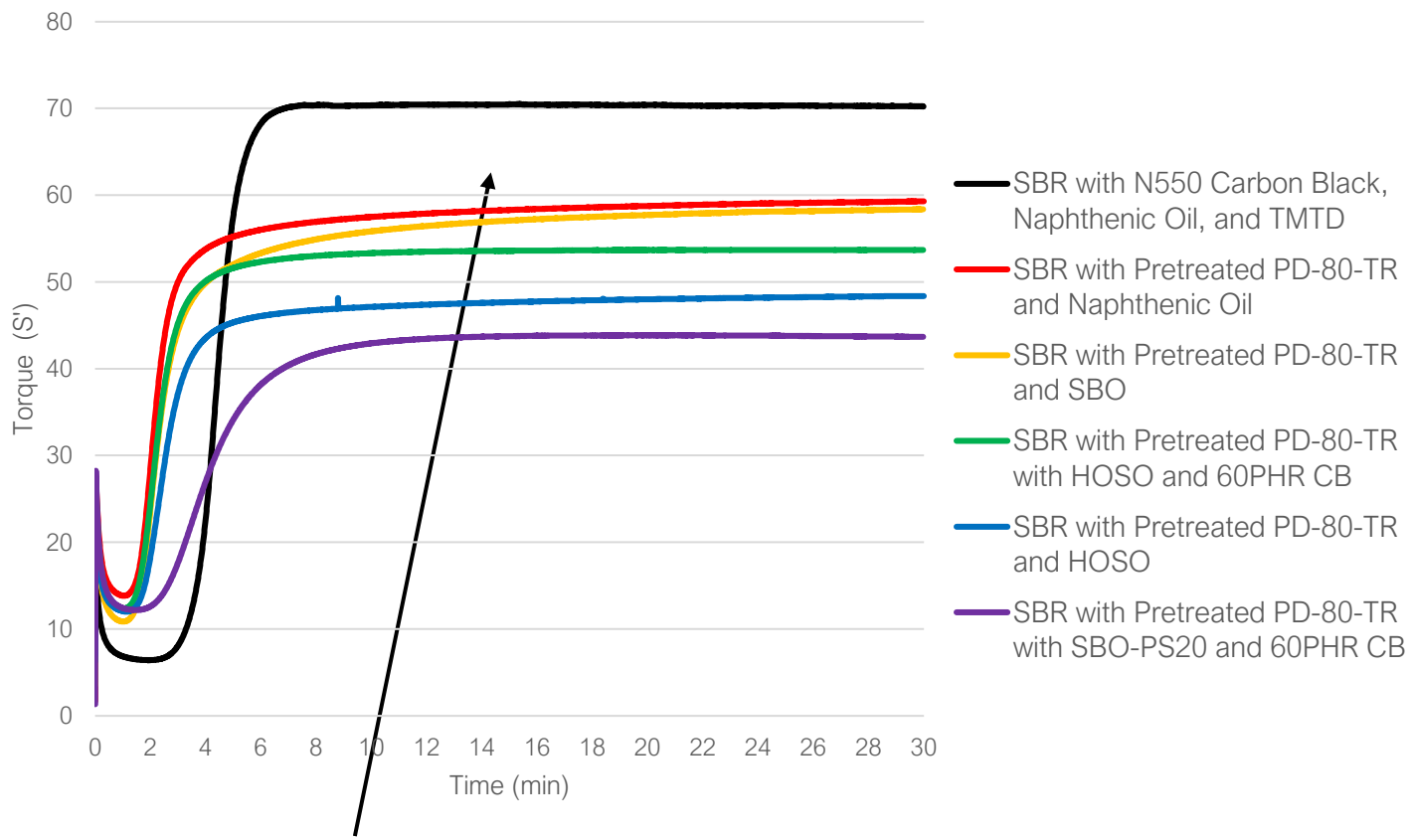




MRP	Particle size, µm	Volatiles (Below 250°C) %	Mineral (SiO2, ZnO), %	Carbon Black, %	Polymer, %	Natural Rubber	Synth. Rubber
PD80-TR	177	4	8	27	61	44	17
PD140-TR	105	4	9	31	55	30	25

- Composition of MRP varies depending on source material (ie. truck vs. passenger car tires)
- Composition of MRP impacts compatibility with new rubber composites (natural vs. synthetic)

Rheology of SBR (PD-80 TR) Samples

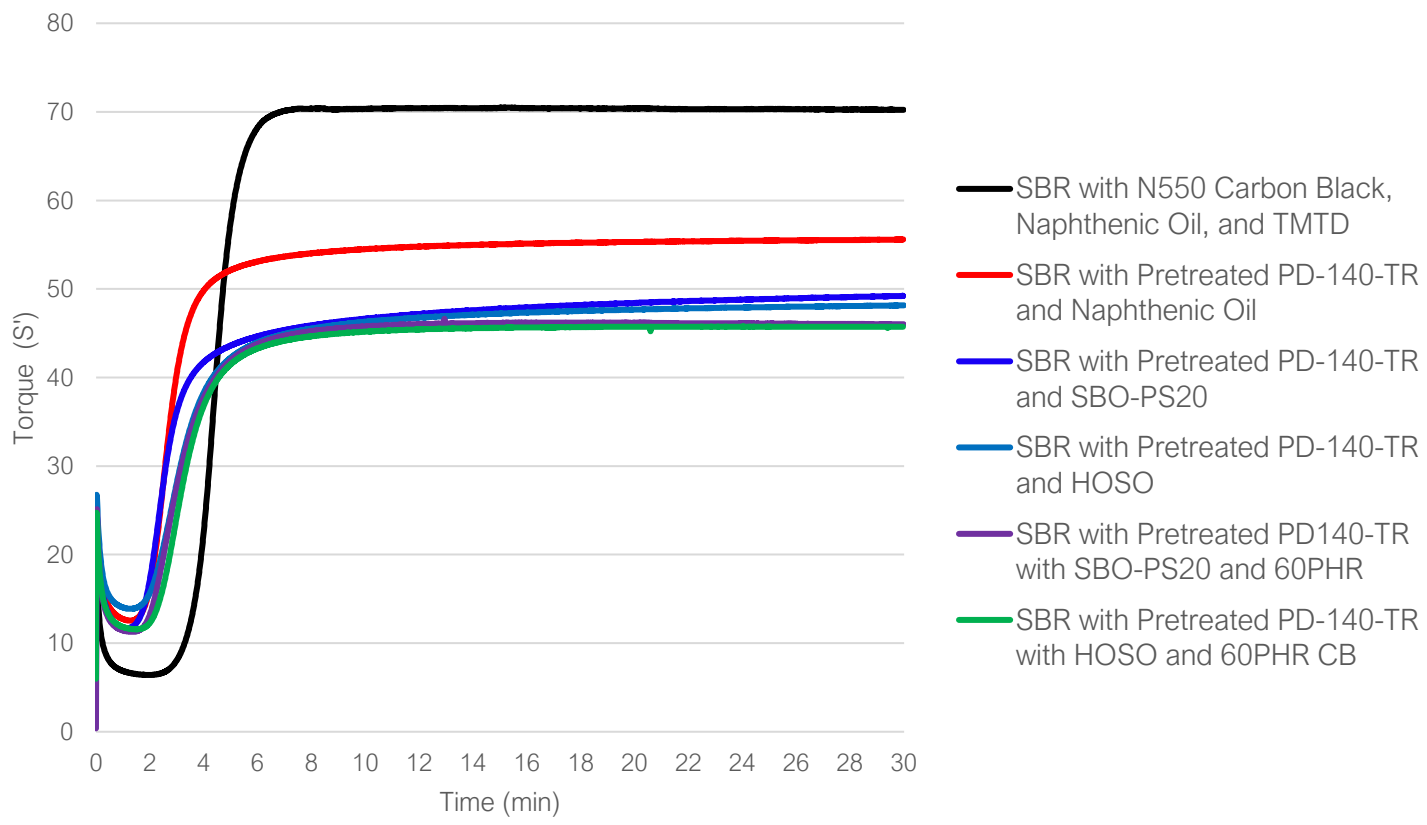


Use of MRP decreases torque and accelerates initial cure rate

SBR	S` Max	Scorch Time (TS 2)	TC 90
SBR with N550 Carbon Black, Naphthenic Oil, and TMTD (Control)	70.49	3.1	5.4
SBR with Pretreated PD-80-TR and Naphthenic Oil	59.29	1.5	4.6
SBR with Pretreated PD-80-TR and HOSO	48.38	1.7	4.5
SBR with Pretreated PD-80-TR with HOSO and 60PHR CB	53.69	1.5	3.8
SBR with Pretreated PD-80 and SBO	58.38	1.5	6.3
SBR with Pretreated PD-80-TR with SBO-PS20 and 60PHR CB	43.86	2.5	7.2

- SBR compounds containing MRP generally exhibit lower scorch time (less processing time)
- Compounds containing HOSO exhibit lower torque

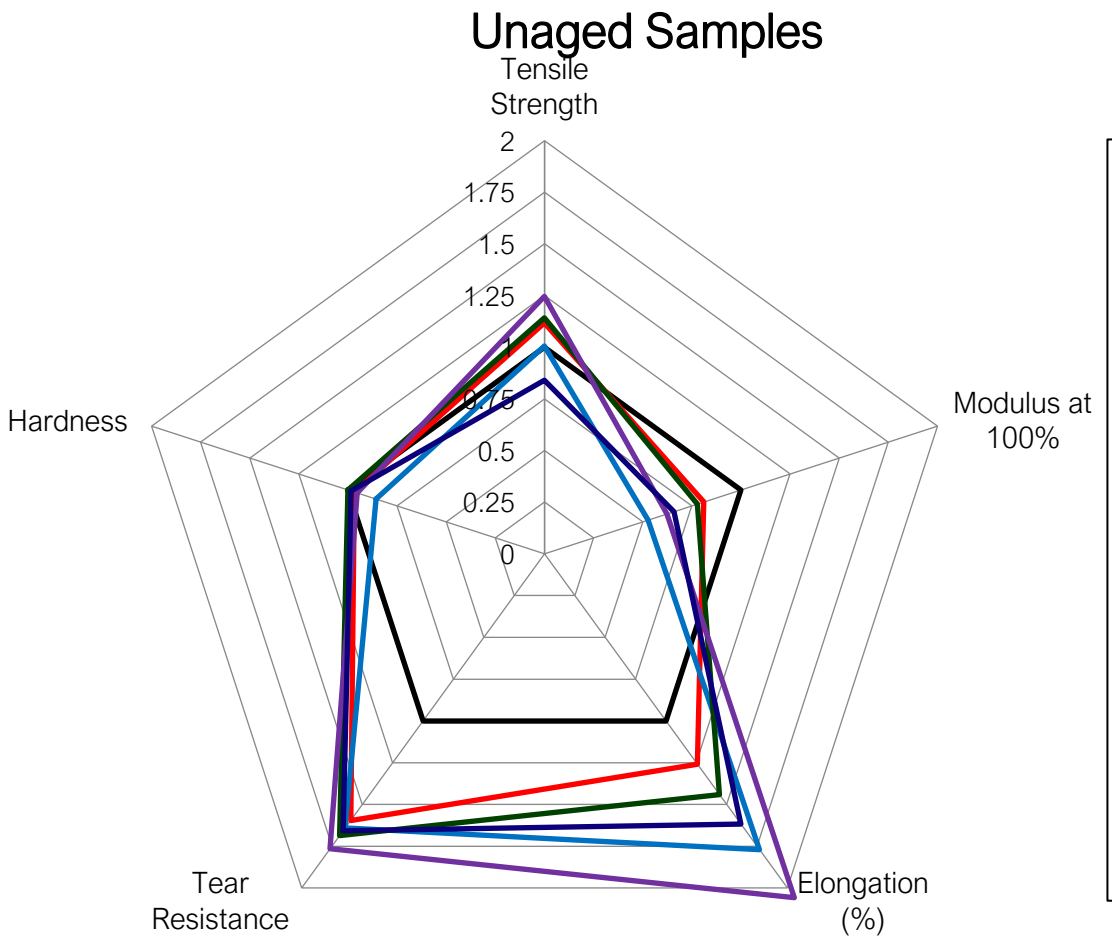
Rheology of SBR (PD-140 TR) Samples

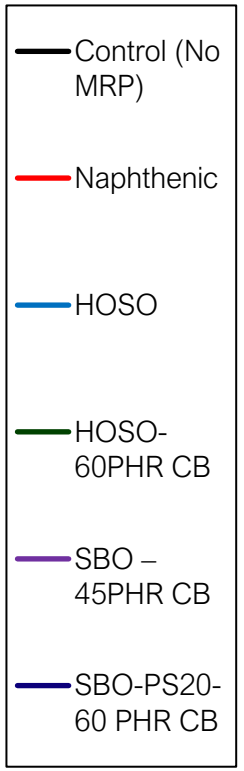


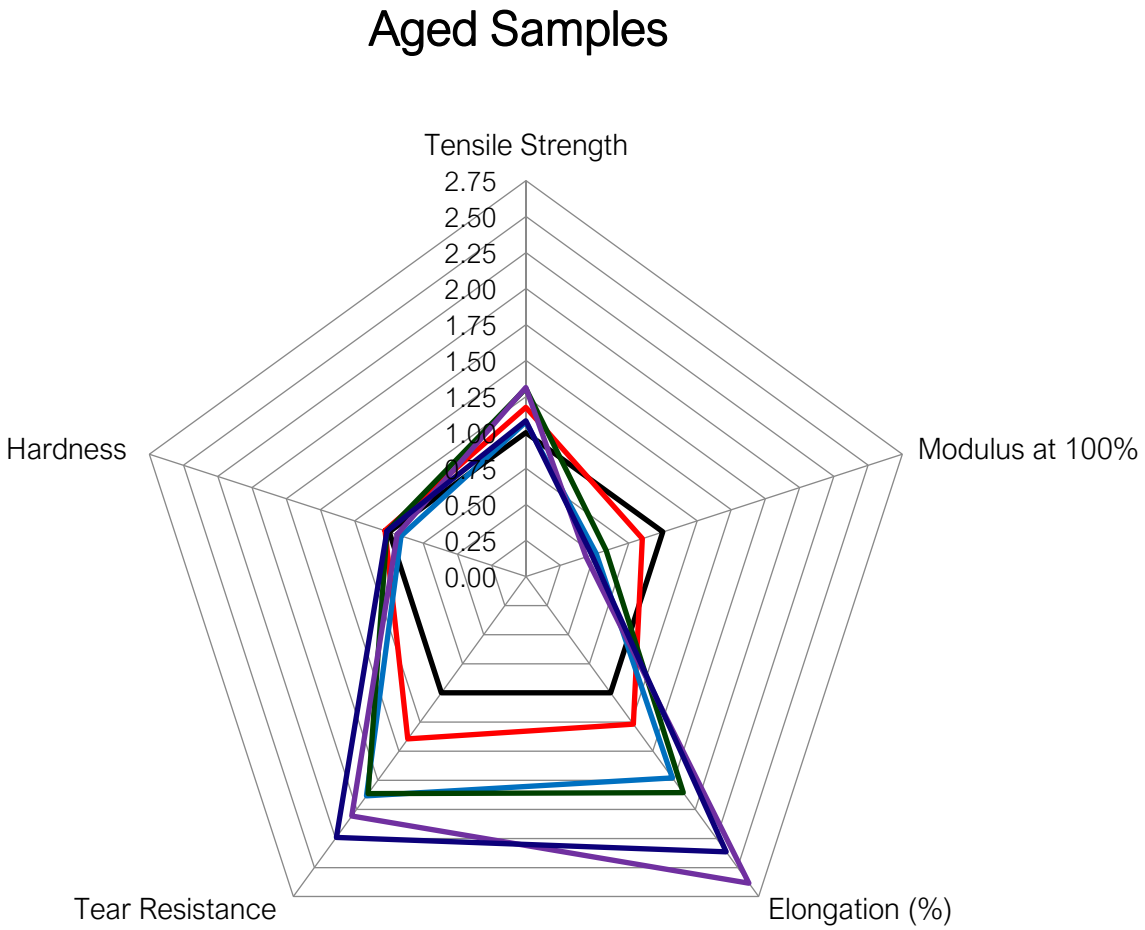
SBR	S` Max	Scorch Time (TS 2)	TC 90
SBR with N550 Carbon Black, Naphthenic Oil, and TMTD (Control)	70.49	3.1	5.4
SBR with Pretreated PD-140-TR and Naphthenic Oil	55.58	1.9	4.5
SBR with Pretreated PD-140-TR and HOSO	48.15	2.0	6.7
SBR with Pretreated PD-140-TR with HOSO and 60PHR CB	45.75	2.2	5.4
SBR with Pretreated PD-140-TR and SBO-PS20	49.22	1.7	7.2
SBR with Pretreated PD140-TR with SBO-PS20 and 60PHR	46.19	2.0	5.3

- All compounds containing soy-based oil exhibit lower torque & faster initial cure (tS2)
- Addition of carbon black does not positively impact cure characteristics

Material Properties of SBR-MRP rubbers (PD80-TR)

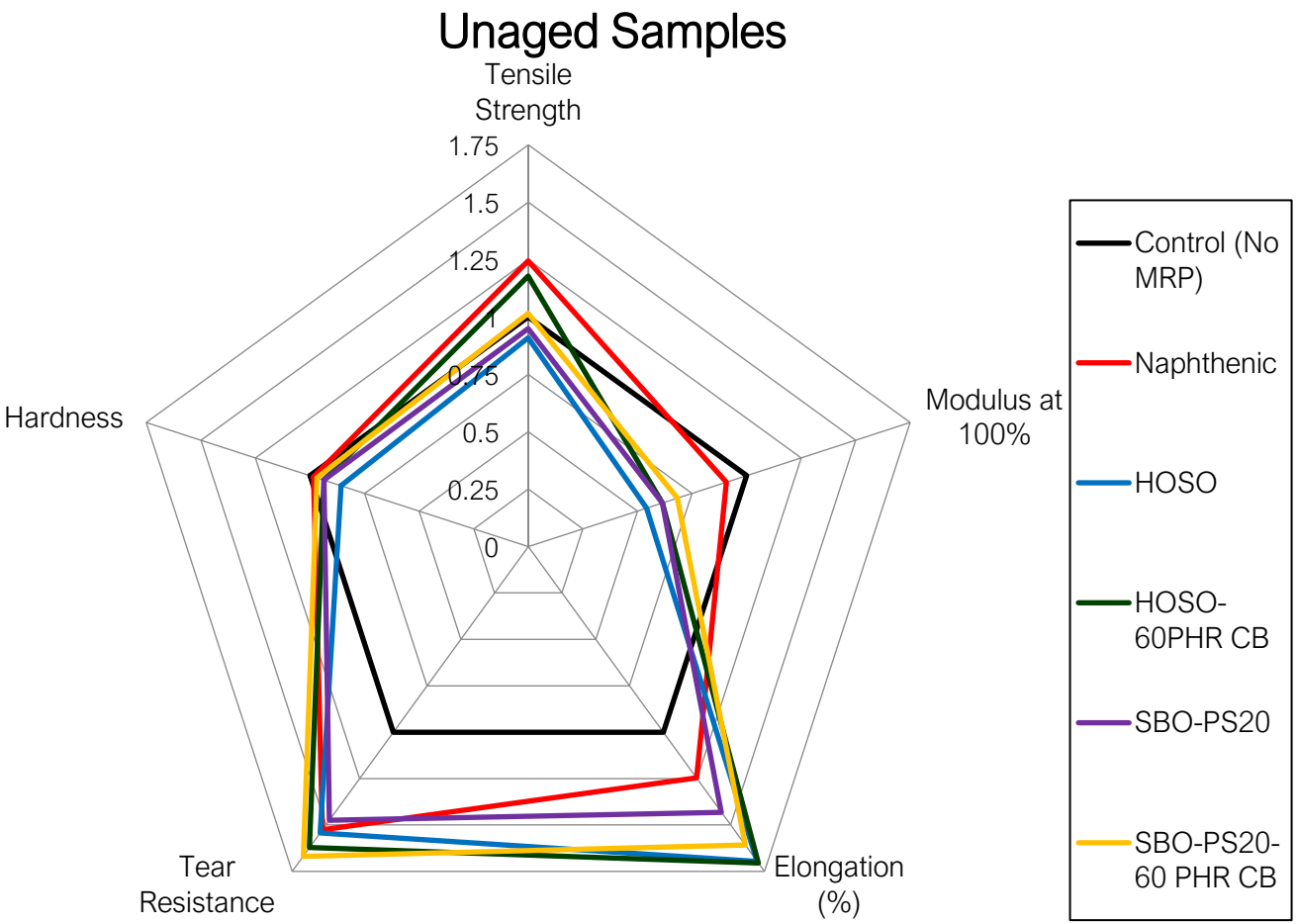


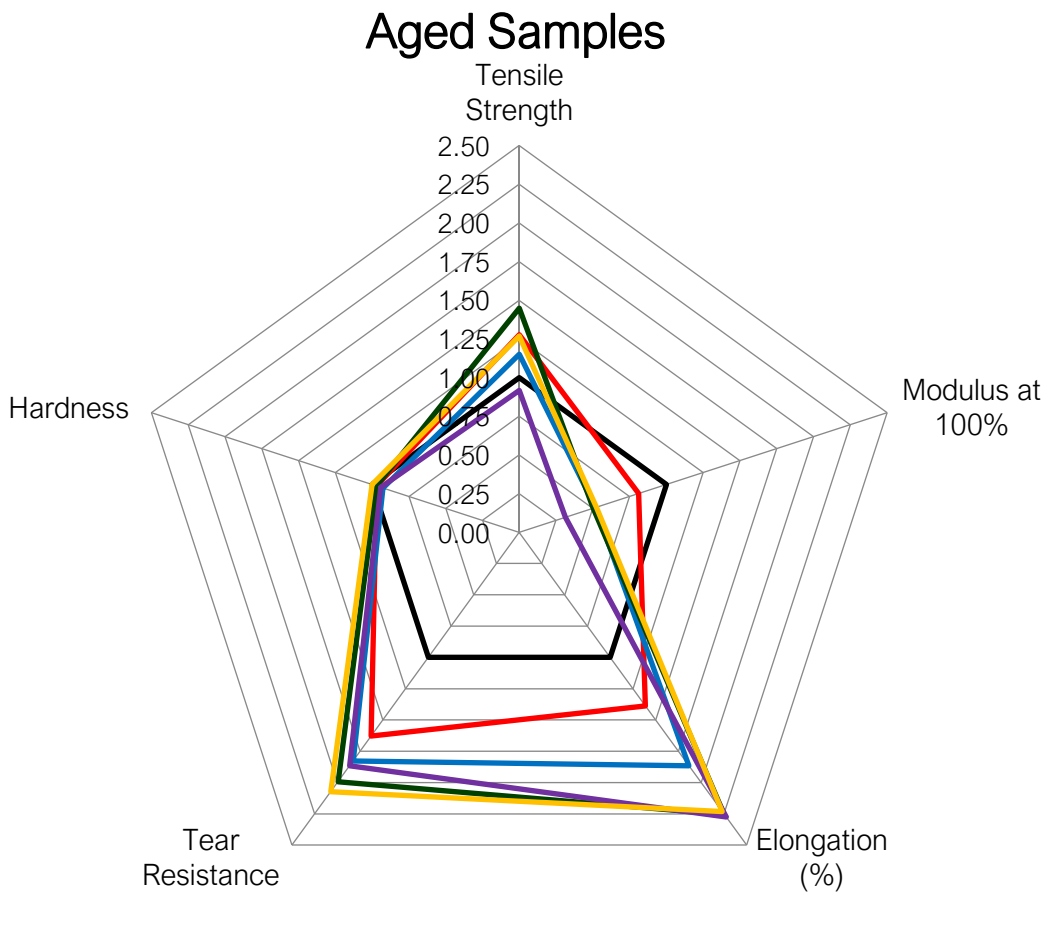




- Compounds with MRP and soy-based oils demonstrate large increase in tear strength and elongation compared to the control
- Compounds with MRP and soy-based oils exhibit lower modulus compared to the control

Material Properties of SBR-MRP rubbers (PD140-TR)





- Compounds with MRP and soy-based oils demonstrate large increase in tear strength and elongation compared to the control
- Compounds with MRP and soy-based oils exhibit lower modulus compared to the control

Material Properties of Optimal SBR Formulations

Oil Used	MRP	Tensile Strength, MPa	Elongation at Break, %	M100 Modulus, MPa	M300 Modulus, MPa	Tear Strength, N/mm	Hardness
Unaged							
Control (No MRP)	-	10.0 ± 0.7	227 ± 22	3.34 ± 0.22	-	22.1 ± 1.9	63
HOSO-60PHR CB	80	11.4 ± 0.2	327 ± 13	2.6 ± 0.13	10.81 ± 0.08	37.3 ± 1.3	63
SBO-45PHR CB	80	12.4 ± 0.6	467 ± 25	2.08 ± 0.05	7.26 ± 0.13	39.0 ± 3.0	60
HOSO-60PHR CB	140	11.7 ± 0.11	387 ± 11	2.05 ± 0.08	9.23 ± 0.23	35.8 ± 2.7	59
SBO-PS20-60 PHR CB	140	10.1 ± 0.11	365 ± 12	2.28 ± 0.07	8.99 ± 0.20	36.9 ± 1.0	61
Aged at 80°C for 7 days							
Control (No MRP)	-	9.2 ± 0.6	134 ± 12	6.32 ± 0.66	-	17.0 ± 0.8	68
HOSO-60PHR CB	80	12.0 ± 0.38	249 ± 20	3.7 ± 0.29	-	31.7 ± 3.3	69
SBO-45PHR CB	80	12.1 ± 0.8	353± 18	2.78 ± 0.10	10.04 ± 0.36	35.0 ± 3.6	64
HOSO-60PHR CB	140	13.4 ± 0.23	302 ± 11	3.18 ± 0.15	13.04 ± 0.10	33.9 ± 3.7	66
SBO-PS20-60 PHR CB	140	11.7 ± 0.25	299 ± 6	3.32 ± 0.08	10.92 ± 1.47	35.3 ± 2.0	68

- Recommended SBR formulations dependent upon type of tire recycled

Conclusions

- SBR containing MRP will possess much lower torque and higher initial vulcanization rates when compared to SBR containing no MRP
  - Increasing amount of carbon black in formulation will have differing results that are highly dependent upon the combination of MRP and processing oil
- Properties of SBR dependent upon combination of MRP and processing oil used
  - For 80MRP, the use of unmodified SBO produces SBR with higher elongation, tensile strength, and tear resistance compared to SBR containing no MRP
  - For 140MRP, using unmodified HOSO with 60PHR of carbon black will produce SBR with optimal performance properties
- Primary benefit of using MRP and soy-based oils is the improvement in tear resistance

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Thank you for your time!