Use of Modified High Oleic Soybean Oil in Automotive EPDM Rubber

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SPE-ACCE

CAN WE MOVE SOCIETY CLOSER TO A CIRCULAR ECONOMY?

With a vehicle typically containing hundreds of different metals, plastics, fabrics and composites, manufacturers are increasingly looking to use renewable and recycled materials that have a reduced life-cycle impact, as long as they provide equivalent or superior performance.

OUR GOAL

We aspire to only use **recycled and renewable plastics** in our vehicles globally

* From Ford 2019 Sustainability Report

Typical Recipes of Foams, Plastics, and Rubber

Foams: ~40lbs/vehicle
- Isocyanate
- *Polyol*
- *Fillers*

Biobased Modifications
- *Polyol*
  - *Soy*
  - *Algae*
  - CO_2
- *Fillers*
  - *Cellulose*

Plastics: ~ 400lbs/vehicle
- Polymer
- *Fillers*

Biobased Modifications
- *Fillers*
  - *Wheat Straw*
  - *Rice Hulls*
  - *Wood Fiber*
  - *Crustaceans*
  - *Biochar*
  - *Agave*

Rubber: ~20lbs/vehicle (non-tire rubber)
- Polymer
- *Fillers*
- *Oil*

Biobased Modifications
- *Fillers*
  - *Eggshells*
  - *Cellulose*
- *Oil*
  - *Soy*

In Production and Targeted for Production

Soy foam – All NA seat backs, seat cushions and headrests (soy polyol)
Soy in rubber – Slap pad on F-150 (soy oil)

Cellulose – Armrest reinforcement on the MKZ
Cellulose/glass fiber hybrid - Console reinforcement on the Continental

Wheat straw - Bin on the Flex

Rice hulls – Electrical bracket on the F-150

31,251 beans/vehicle
510 M soybeans!
20+ Million vehicles
251 M lbs CO_2 reduction

Images
*aicr.org
*Bioplastics News
*haystraws.com
*ricehull.com

Project Goal

Goal: Develop automotive EPDM rubber formulations that contain soybean oil as a processing oil.

Potential Benefits:

- Approximately 14 lbs of EPDM rubber used in automotive parts per vehicle. Increasing the sustainable content of those parts is a corporate goal.
- High oleic soybean oil has a higher heat resistance than degummed soybean oil and may improve the aging performance of the EPDM parts.

Challenges:

- Incompatible polarity levels of the EPDM rubber and soybean oil can make the formulation challenging.
- Low petroleum oil prices make the business case for soybean oil challenging.

What makes an EPDM rubber?

Base Polymer Material

- Ability to deform and recover

Vulcanizing Agents (Sulfur or Peroxide)

- 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)

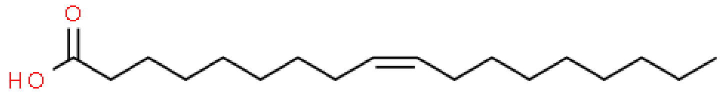
- Mechanically reinforce rubber
- Improves wear and physical properties

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

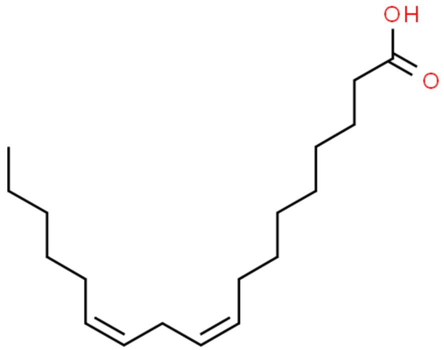
Why Modify High Oleic Soybean Oil?

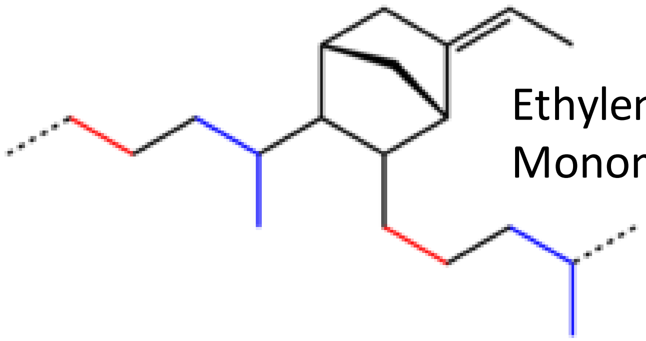
- High oleic soybean oil is more thermally stable when compared to unmodified soybean oil, making it suitable for use in processing EPDM material
  - Oleic acid has fewer double bonds in structure than linoleic acid, limiting areas of oxidative impact
- However, EPDM polymer base has a higher viscosity compared to unmodified high oleic soybean oil
  - Non-compatible structures leads to issues with oil bleed-out
- Chemical modification of high oleic soybean oil structure leads to increase unsaturation and viscosity
  - Improve compatibility and crosslinking with EPDM rubber
  - Maintain thermal stability seen in unmodified HOSO



Oleic Acid

Linoleic Acid





Ethylene Propylene Diene Monomer (EPDM) Rubber

Formulation of EPDM Rubber 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 15 PHR
  - **5.2-5.3% by weight** of total compound
- Either sulfur or peroxide are used as vulcanizing agents based on the formulation
  - In EPDM vulcanized with peroxide, two different coagents are used in tandem with a vulcanizing retardant (Antioxidant DQ) in varying concentrations
    - Triallyl Isocyanurate (TAIC)
    - Trimethylolpropane Diallyl Ether (TMPDE)
- The following oils were tested
  - Paraffinic (control)
  - High oleic soybean oil
  - Functionalized high oleic soybean oil
  - Functionalized high oleic soybean gel

Examples of EPDM Recipes

Sulfur Cured

Purpose	ingredient name	phr
Rubber Base Material	Keltan ECO 5740	26.70
	Royalene 694*	128.30
Plasticizer	High Oleic Soybean Oil	15.00
Reinforcing Filler	N550 Carbon Black	105.00
Vulcanization Activators	Zinc Oxide	5.00
	Stearic Acid	1.50
Vulcanization Accelerators	Tuex/TMTD	1.00
	BZ/BZX	1.80
	Naugex MBTS	3.00
Vulcanizing Agent	Sulfur	0.80
	Total	288.10

Peroxide Cured

Purpose	ingredient name	phr
Rubber Base Material	Keltan ECO 5740	26.70
	Royalene 694*	128.30
Plasticizer	High Oleic Soybean Oil	15.00
Reinforcing Filler	N550 Carbon Black	105.00
Vulcanization Activators	Zinc Oxide	5.00
	Stearic Acid	0.50
Vulcanization Coagent	Triallyl Isocyanurate	1.00
Vulcanization Retardant	Antioxidant DQ	1.00
Vulcanizing Agent	Peroxide	3.00
	Total	285.50

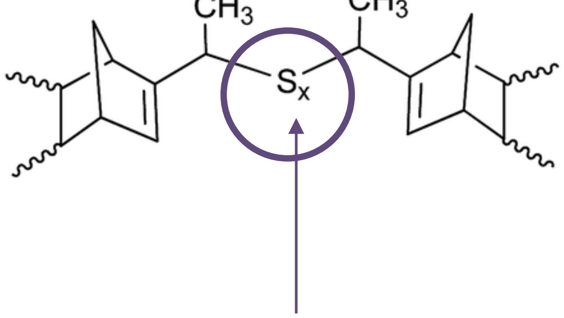
*Note: Royalene 694 contains 100 phr EPDM and 75 phr paraffinic oil

Evaluation of EPDM Rubber in the Lab

- Rheometry
- Tensile Properties
- Shore A Durometer
- Crosslink Density Testing
- Compression Set

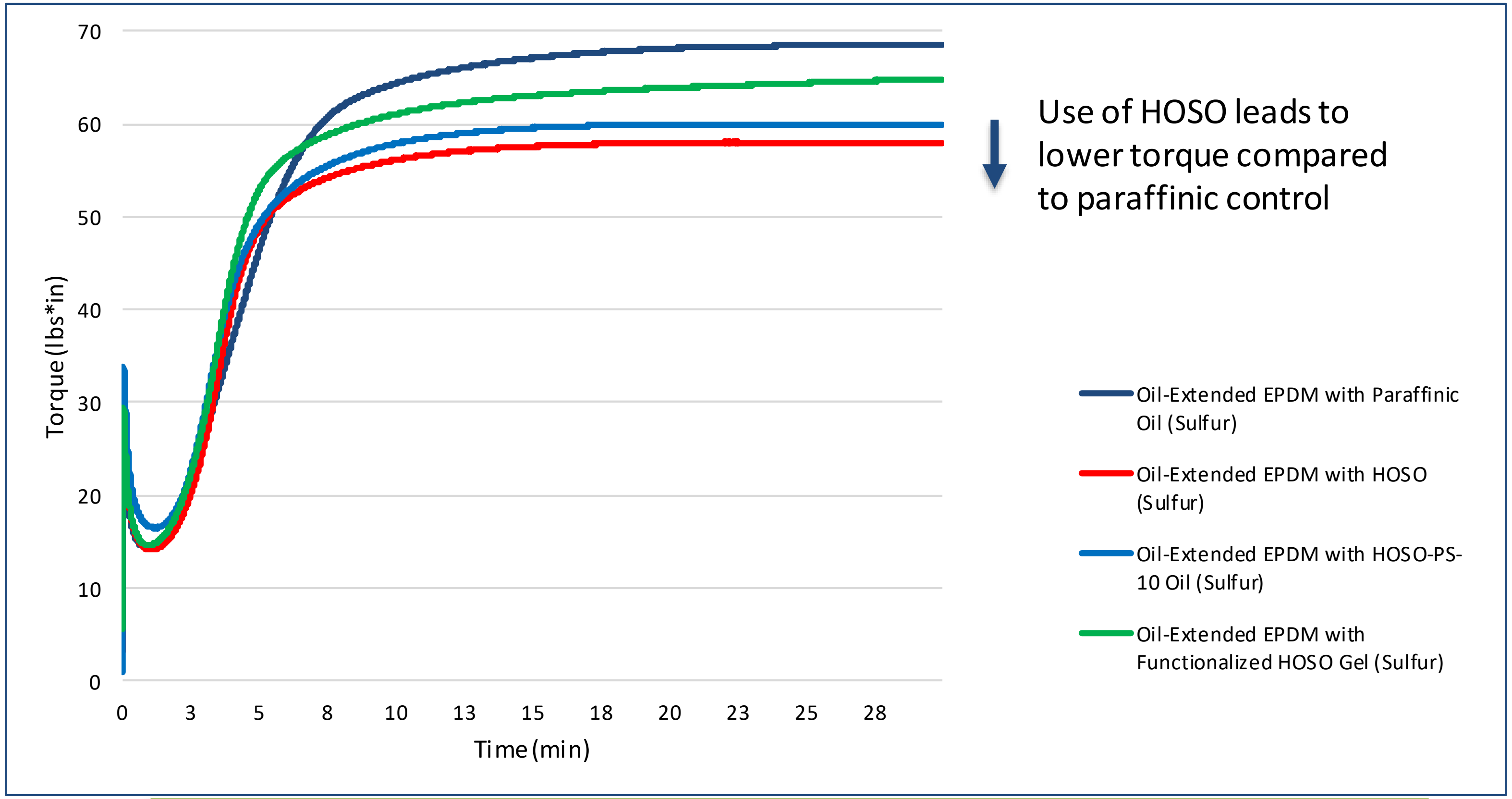
Why use sulfur as curing agent in EPDM?

- Creation of sulfide bridge within EPDM structure
  - Increased crosslinking of intramolecular chains
  - Higher plasticity of resulting material, with resulting increase in tensile strength and elongation
  - Prone to chemical attack, as well as creep and compression set
- Potential areas where sulfur-cured EPDM can be utilized in the vehicle
  - Door seals
  - Window seals
  - Grommets
  - Hoses



Crosslink - Sulfide Bridge

Rheometry of Sulfur-cured EPDM

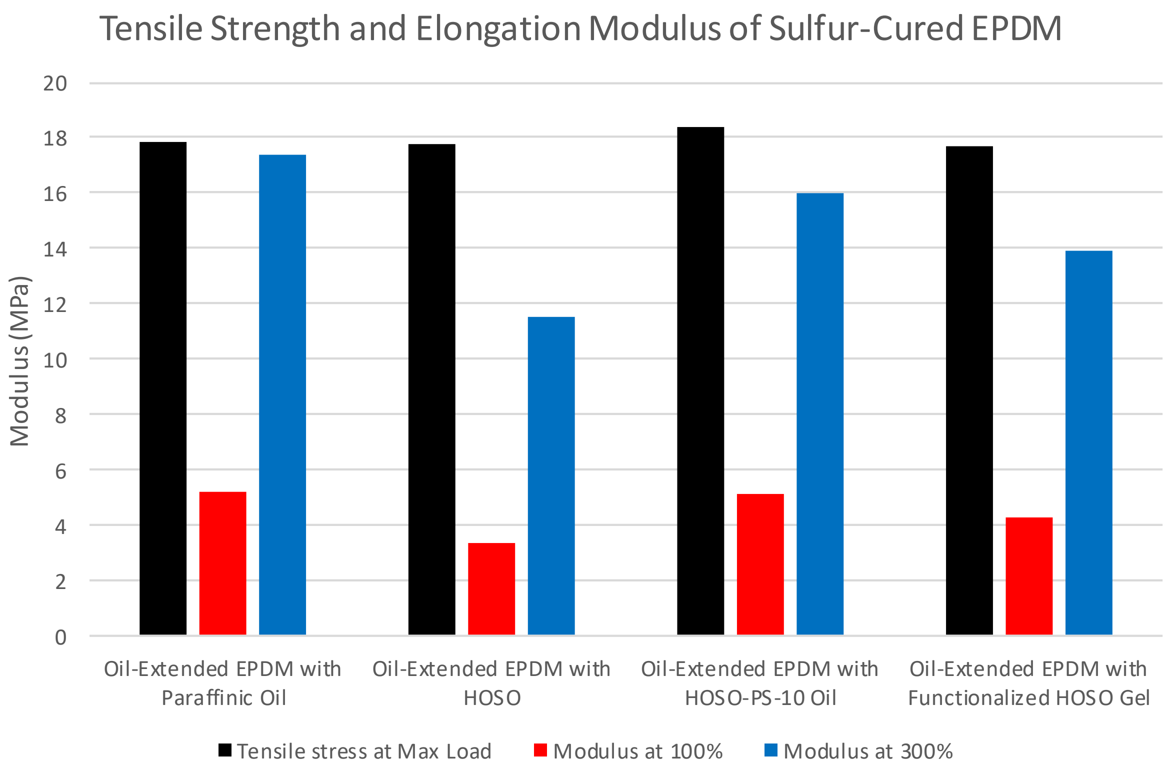


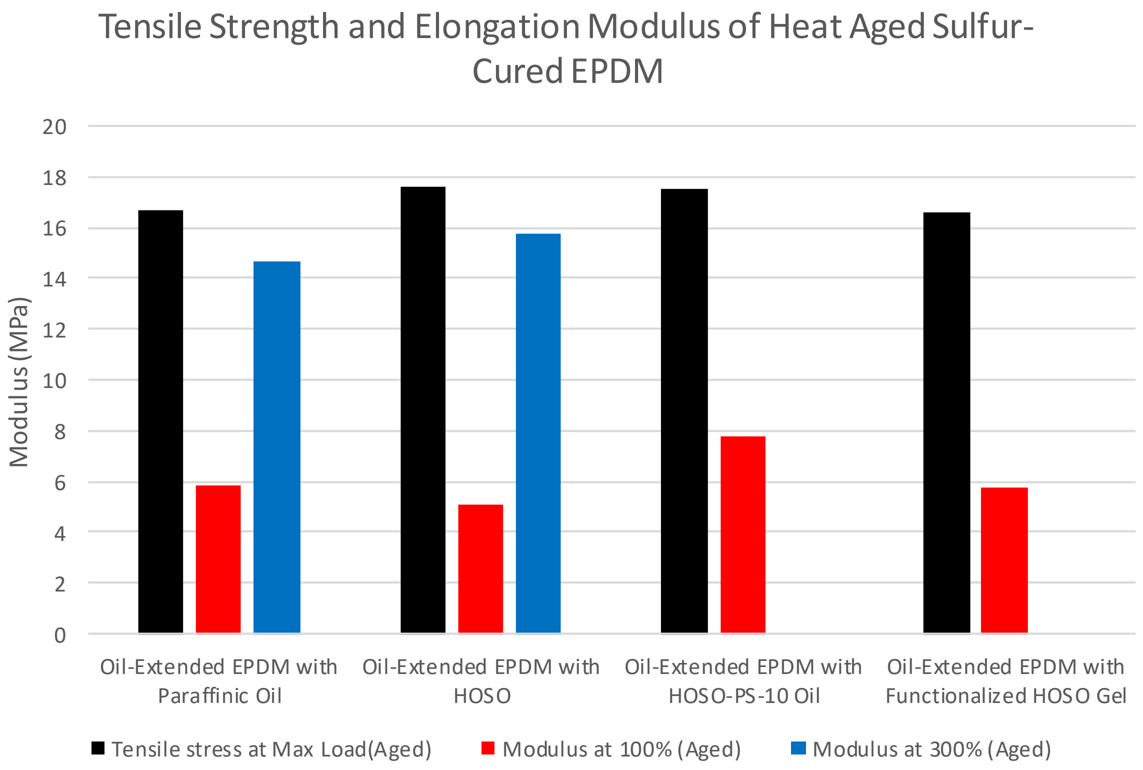
EPDM	S` Max	Scorch Time (TS 2)	TC 90
Oil-Extended EPDM with Paraffinic Oil (Sulfur)	68.56	1.76	8.81
Oil-Extended EPDM with HOSO (Sulfur)	58.05	1.91	7.02
Oil-Extended EPDM with HOSO-PS-10 Oil (Sulfur)	60.02	1.99	7.6
Oil-Extended EPDM with Functionalized HOSO Gel (Sulfur)	64.86	1.77	8.44

- All samples have similar scorch times, independent of processing oil used.

Modified HOSO oils and gels possess higher torque compared to EPDM containing non-modified HOSO but have lower torque relative to the control (paraffinic)

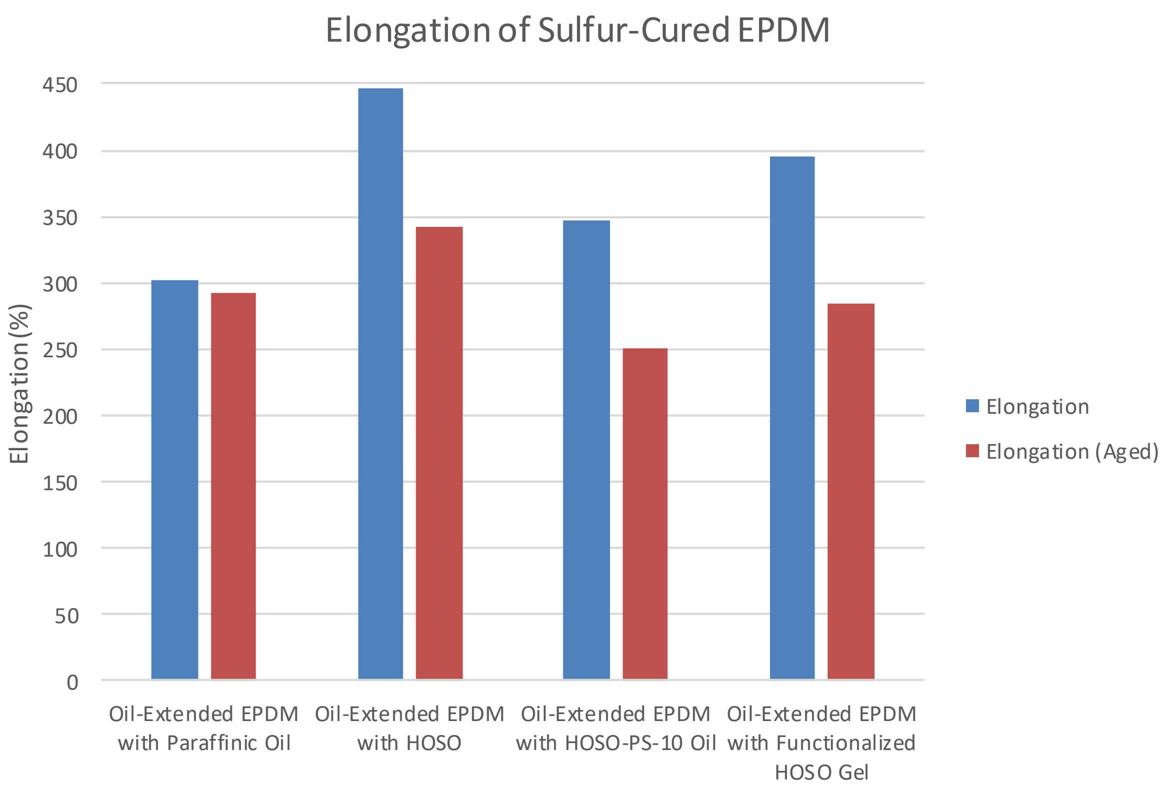
Tensile Properties of Sulfur-cured EPDM

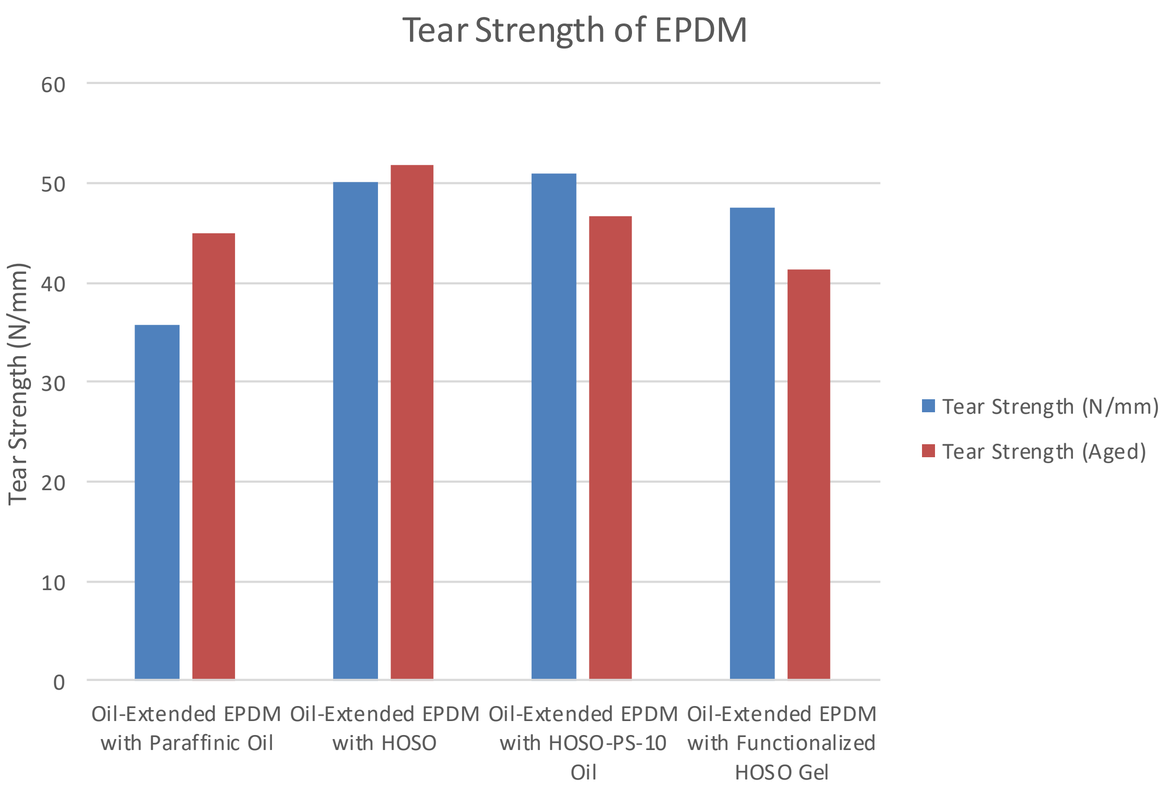




- Unmodified HOSO leads to considerable drop in unaged modulus, but comparable tensile strength to paraffinic oil samples. In the aged state the unmodified HOSO performs equivalently to the paraffinic control.
- Modified HOSO (oil and gel) improves the modulus of the material compared to unmodified HOSO in the unaged state but results in a very stiff material in the aged state.

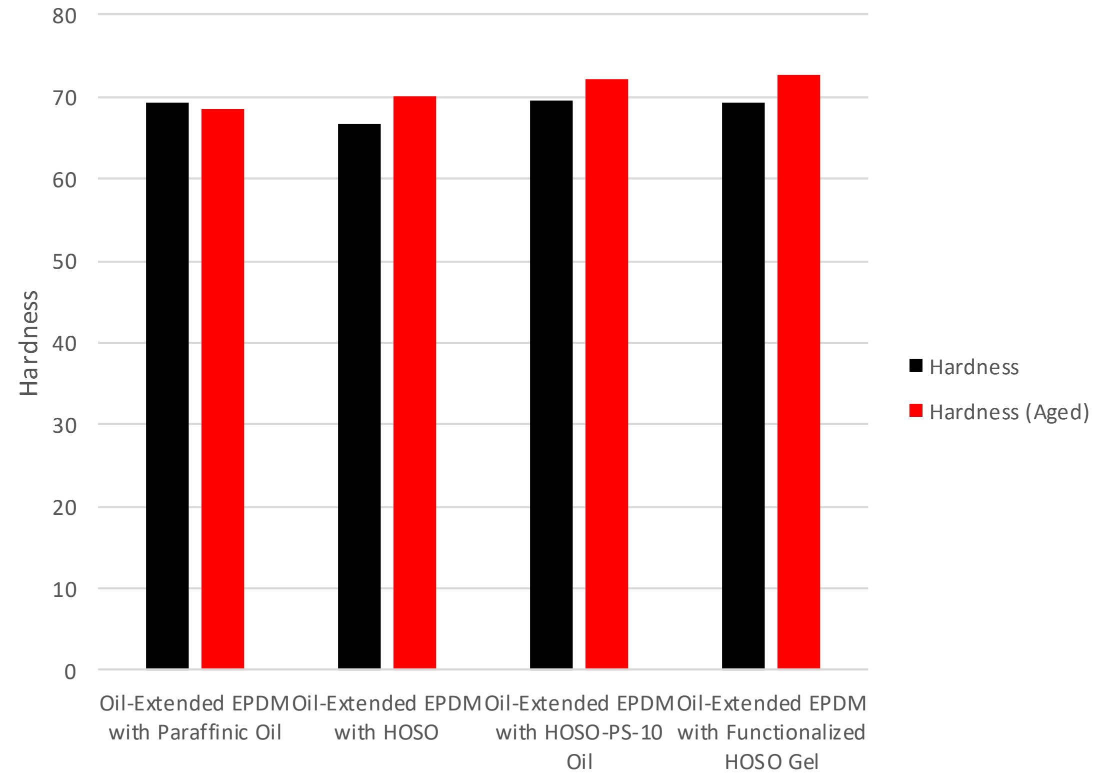
Elongation and Tear Strength of Sulfur-cured EPDM





- Use of unmodified HOSO creates an elastic compound while modified HOSO stiffens the compound compared to unmodified HOSO.
- All HOSO samples produce different elongation results between the unaged and aged states.
- Generally the tear strength improves when using HOSO.

Hardness and Compression Set Resistance of Sulfur-cured EPDM

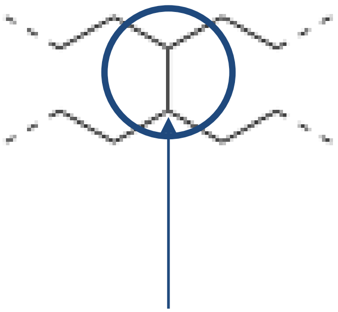


	Compression Set (%)
Oil-Extended EPDM with Paraffinic Oil	17.7
Oil-Extended EPDM with HOSO	34.3
Oil-Extended EPDM with HOSO-PS-10 Oil	23.9
Oil-Extended EPDM with Functionalized HOSO Gel	26.2

- Hardness does not significantly change with the use of HOSO.
- Unmodified HOSO adversely effects EPDM resistance to compression set.
- Modifying HOSO improves compression set compared to unmodified HOSO, but does not match performance of paraffinic control.

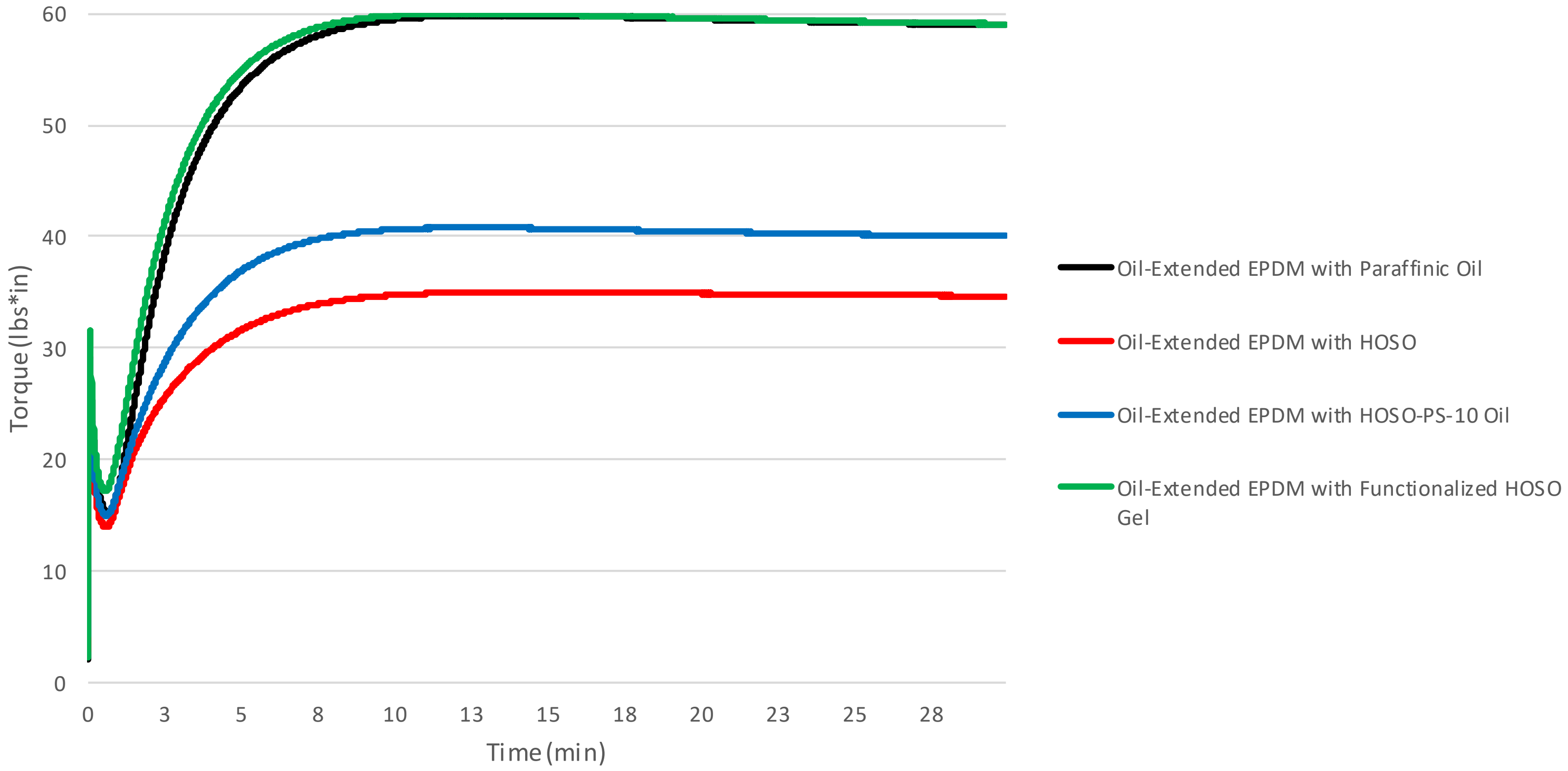
Can peroxide cure provide advantages in comparison to sulfur-cured EPDM?

- Produce carbon-carbon bonds for crosslinking instead of sulfide bridges
  - More resistant to deterioration via heat and chemical attack
  - Creation of bond that is less flexible than sulfur crosslinking, decreasing tear and abrasion resistance
  - Stiffer material also more resistant to compression set, but more marked tensile stress failure
- Potential areas where peroxide-cured EPDM can provide added benefits
  - Hoses
    - Air Conditioner
    - Radiator
    - Brake
  - Wiring and cables



Crosslink – Carbon-Carbon bonds

Rheometry of Peroxide-cured EPDM

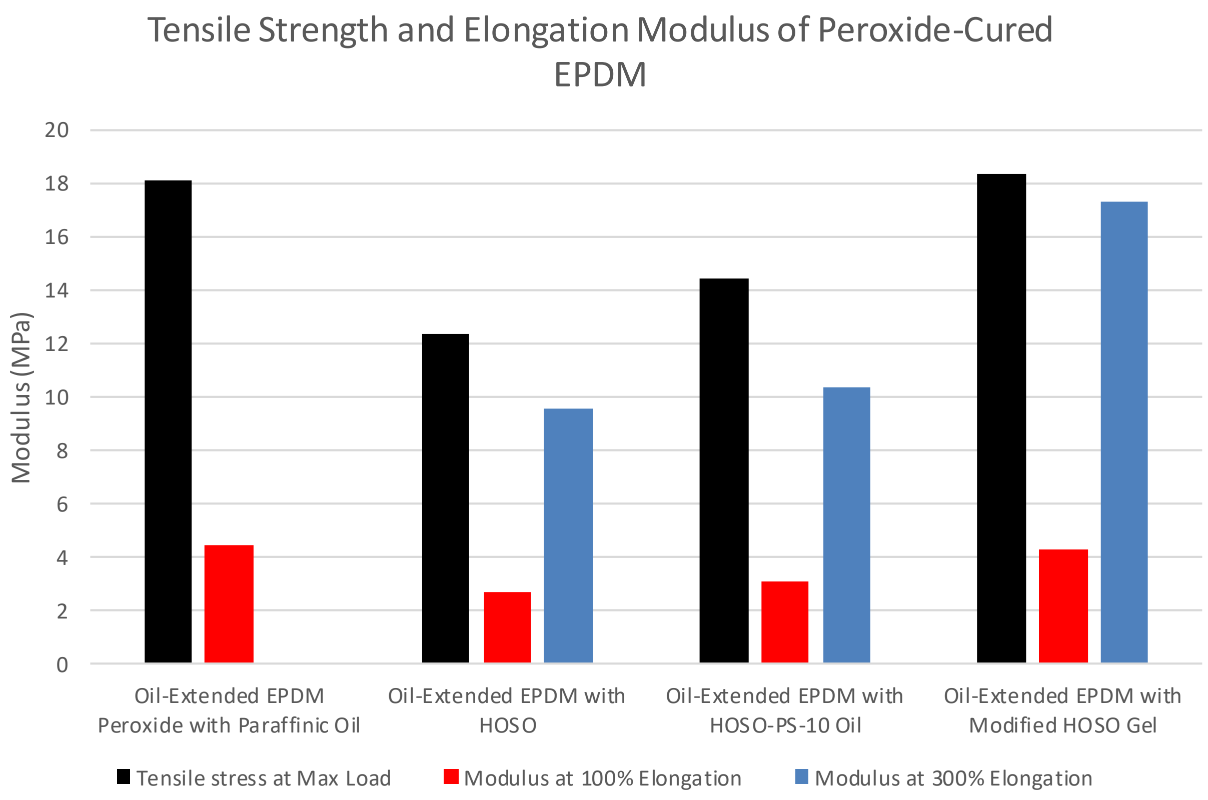


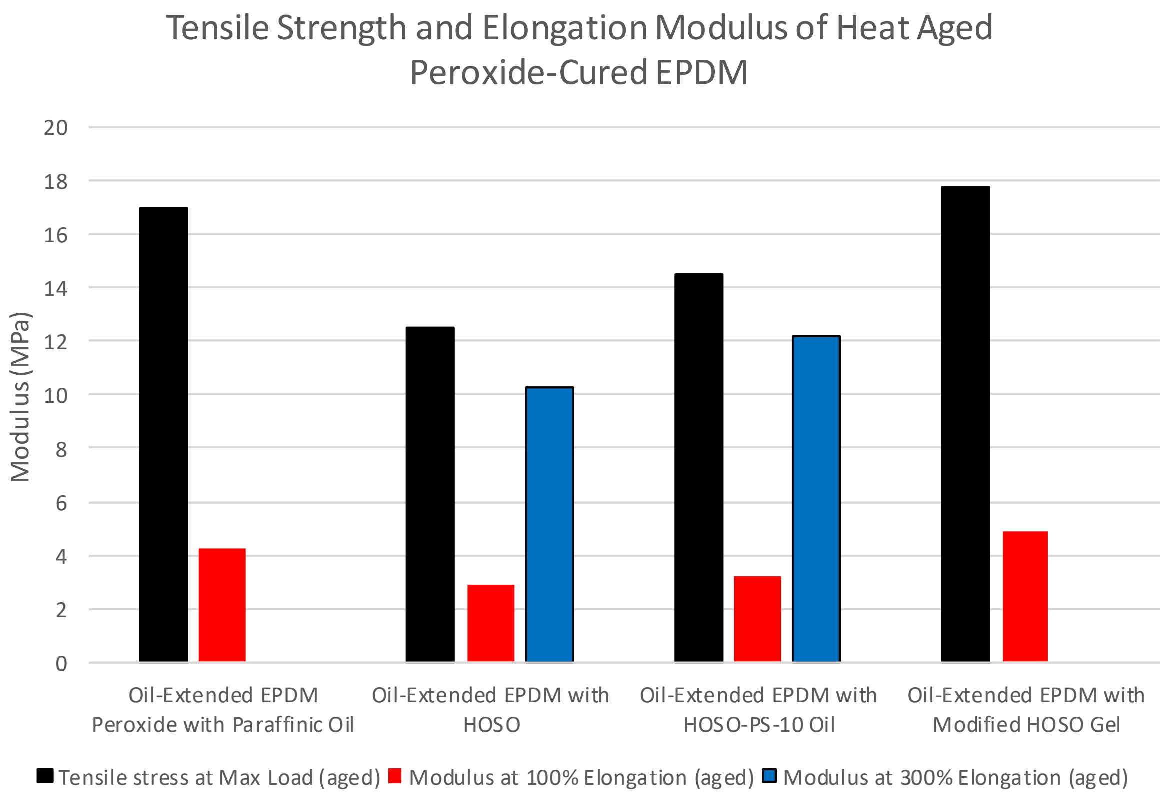
EPDM	S` Max	Scorch Time (TS 2)	TC 90
Oil-Extended EPDM with Paraffinic Oil	59.87	0.97	5.75
Oil-Extended EPDM with HOSO	35	0.94	6.08
Oil-Extended EPDM with HOSO-PS-10 Oil	40.79	0.95	5.8
Oil-Extended EPDM with Functionalized HOSO Gel	60.05	0.85	5.34

- Use of HOSO leads to decrease in torque, indicating lower rigidity.

- EPDM containing HOSO gel possesses substantially higher torque than other HOSO samples (comparable to paraffinic oil), as well as lower scorch time.
- All samples have faster scorch times compared to sulfur-cured samples.

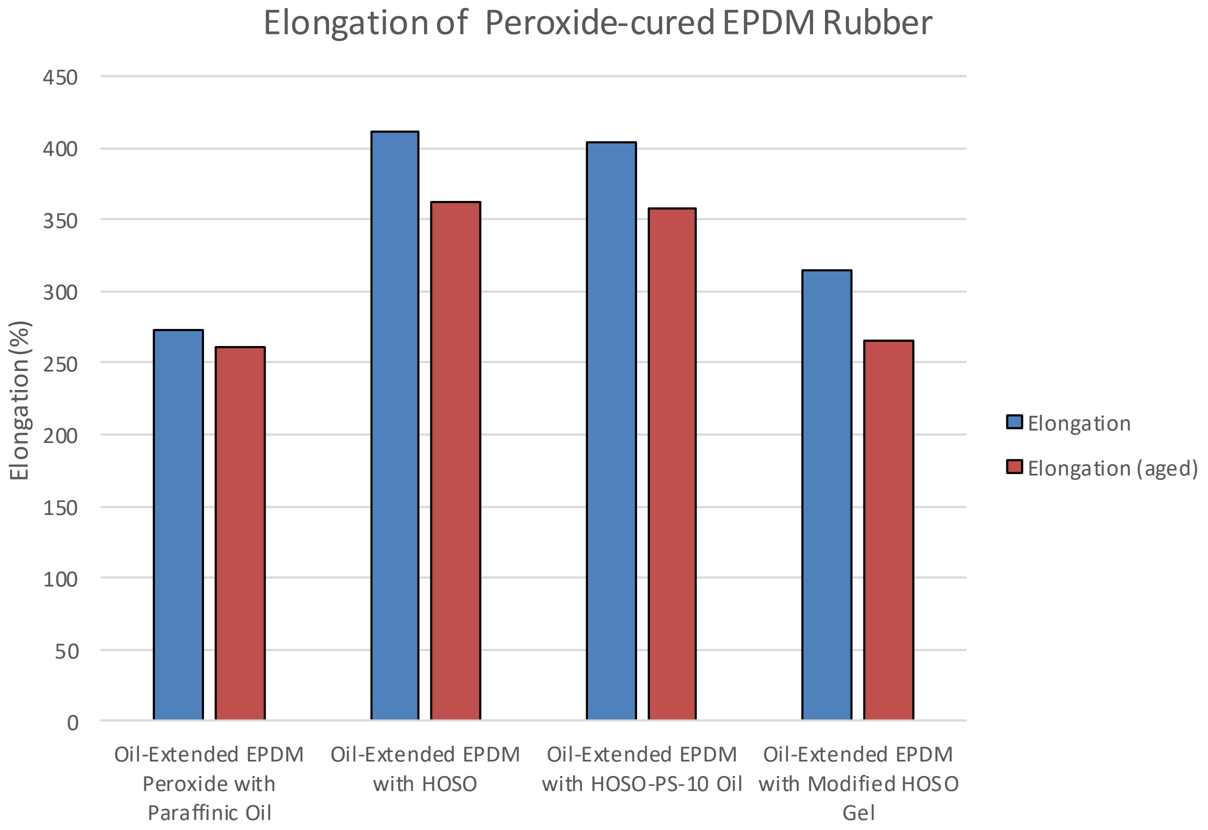
Tensile Properties of Peroxide-cured EPDM

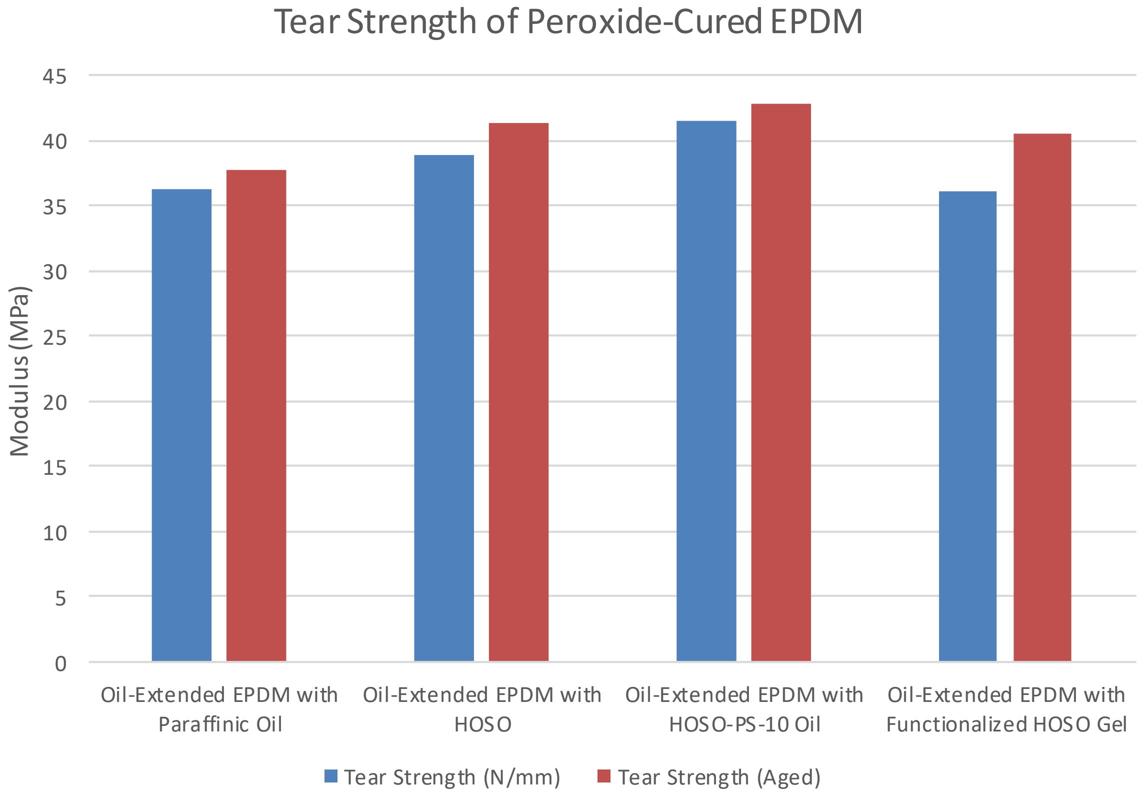




- Use of modified HOSO (oil or gel) will produce EPDM with higher tensile strength compared to unmodified HOSO.
- EPDM containing modified HOSO gel possesses tensile strength and initial modulus (at 100%) most similar to paraffinic oil control material.

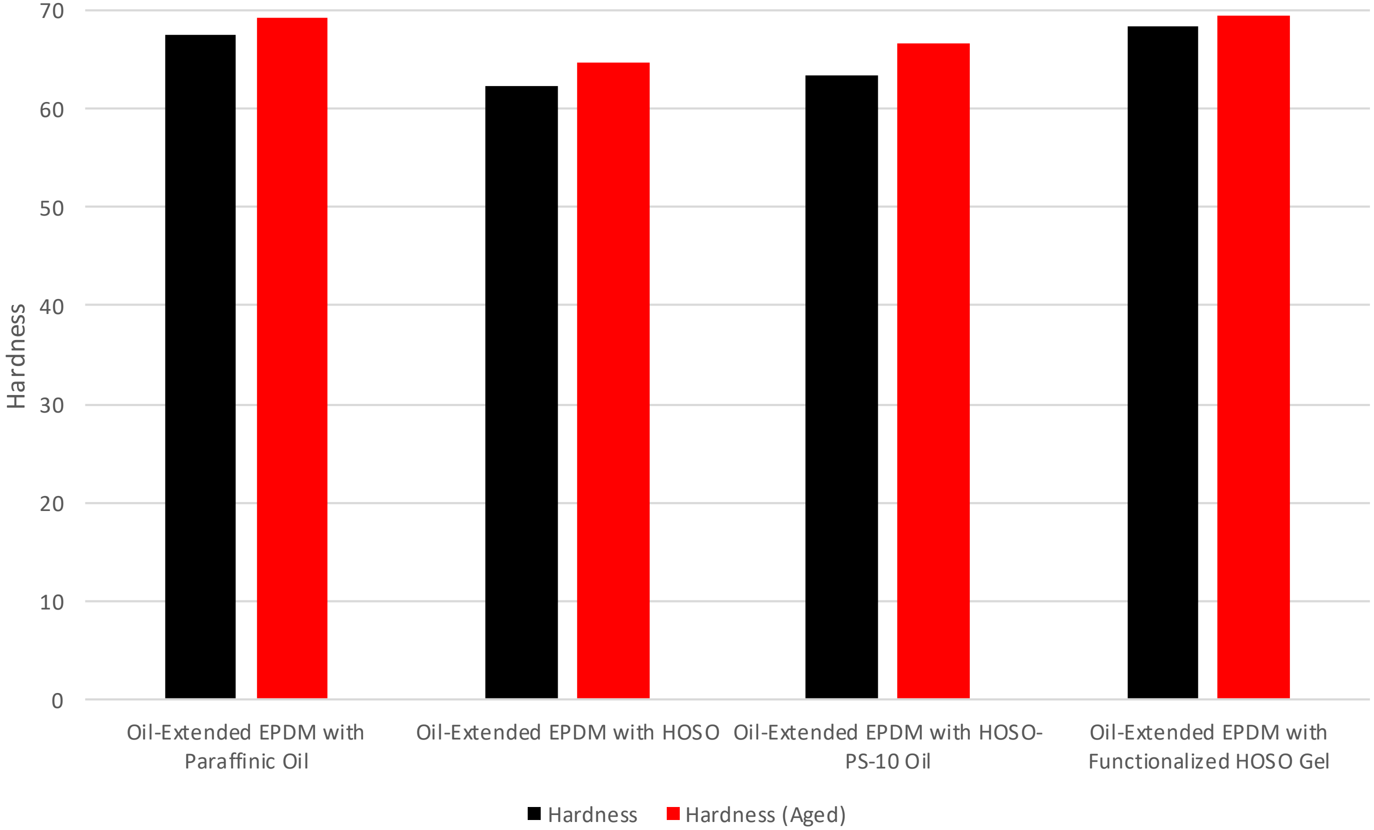
Elongation and Tear Strength of Peroxide-cured EPDM





- Use of any HOSO leads to a more elastic and tear resistant EPDM compared to paraffinic oil control.
- Modification of HOSO in oil form produces EPDM most similar in elongation to EPDM containing unmodified HOSO, with higher tea r resistance.

Hardness and Compression Set Resistance of Peroxide-cured EPDM

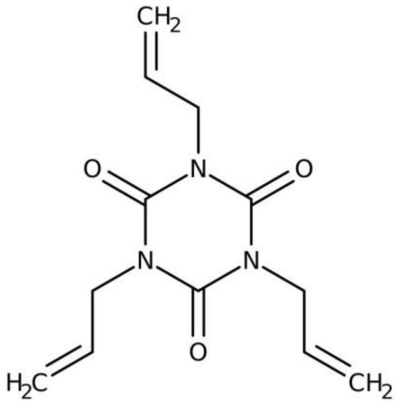


	Compression Set (%)
Oil-Extended EPDM with Paraffinic Oil	17.0
Oil-Extended EPDM with HOSO	35.4
Oil-Extended EPDM with HOSO-PS-10 Oil	36.3
Oil-Extended EPDM with Functionalized HOSO Gel	12.7

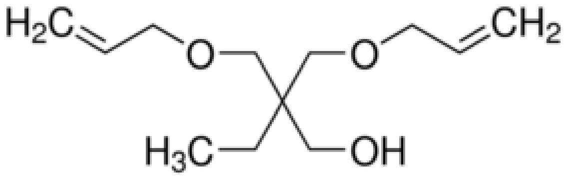
- Use of HOSO in any state will have minimal impact on hardness of resulting EPDM.
- The use of HOSO will have an adverse impact on resulting compression set resistance unless modified HOSO gel is used.

How do additives improve properties of peroxide-cured EPDM?

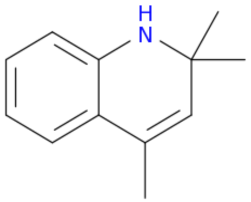
- Coagents – polymerizable multifunctional monomers
  - Used to enhance curing characteristics and performance of resulting EPDM
  - Increases rate of polymerization and crosslinking
  - Tend to have higher modulus and faster scorch time, as well as lower elongation and compression set
  - Examples: Triallyl Isocyanurate (TAIC), Trimethylolpropane Diallyl Ether (TMPDE)
- Antioxidants – react with polymeric free radicals during production
  - Stops the spread to oxidation within polymers
  - Can enhance degradation resistance of resulting EPDM material
  - Potential tool in increasing scorch time and decreasing cure rate
  - Examples: secondary amines, phenolics (DQ), phosphites



TAIC



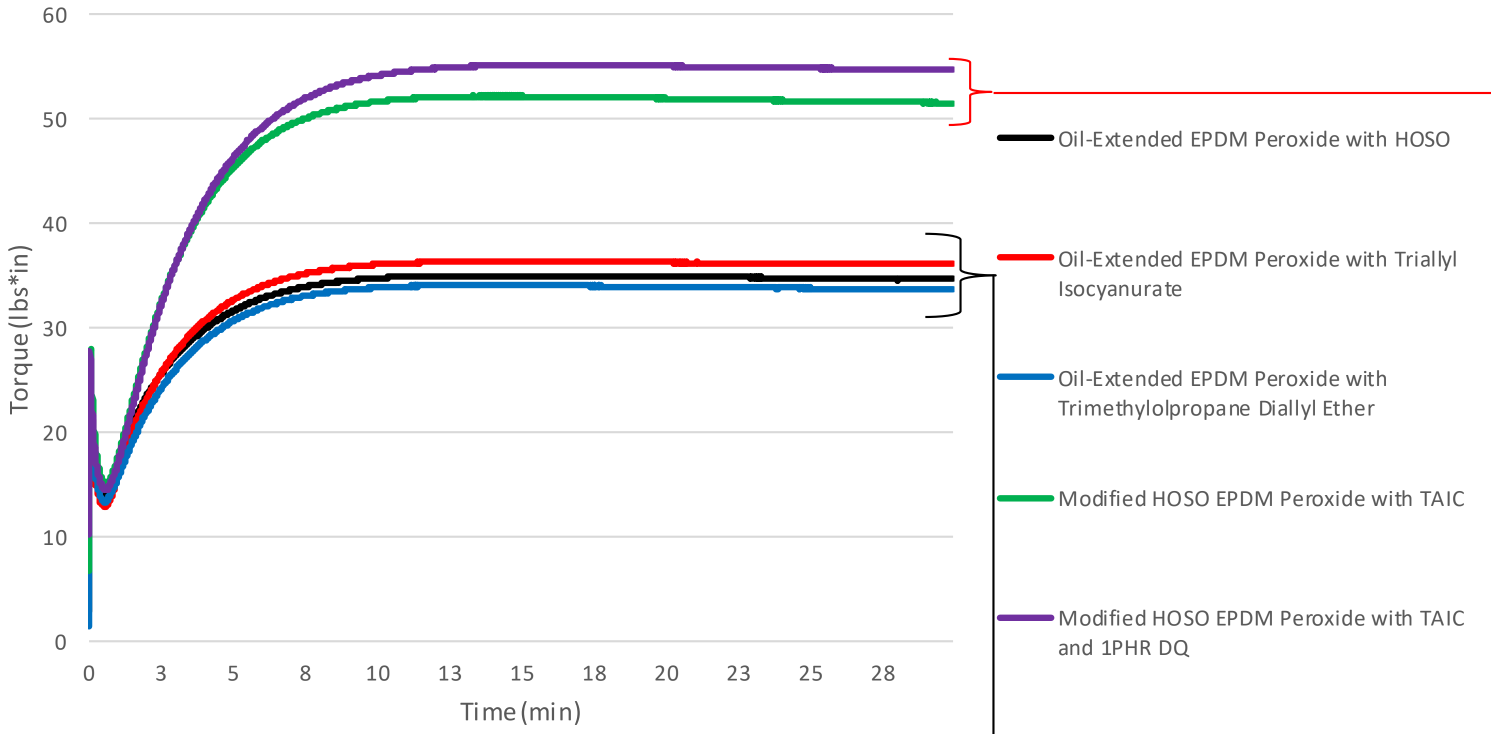
TMPDE



Antioxidant DQ

Goal: Increase the scorch time of peroxide-cured EPDM.

Rheometry of Peroxide-cured EPDM Containing Coagents and Antioxidants



- EPDM containing modified HOSO and TAIC possesses substantially higher torque, but similar cure rate.

EPDM	S` Max	Scorch Time (TS 2)	TC 90
Oil-Extended EPDM Peroxide with HOSO	35	0.94	6.08
Oil-Extended EPDM Peroxide with HOSO and TAIC	36.33	0.91	6
Oil-Extended EPDM Peroxide with HOSO and TMPDE	34.07	0.97	6.09
Modified HOSO EPDM Peroxide with TAIC	52.19	0.95	6.33
Modified HOSO EPDM Peroxide with TAIC and 1PHR DQ	55.16	0.94	6.92

- EPDM containing unmodified HOSO and either TAIC or TMPDE possesses similar torque values and cure rates.

- The use of TAIC, TMPDE, and DQ will not have an effect on scorch times or torque.

Conclusions

- Use of modified HOSO in both sulfur and peroxide-cured EPDM provides material benefits
  - Increase in tensile strength and elongation when compared to unmodified HOSO EPDM
  - Use of modified HOSO oil (PS-10) serves as good potential processing aid in EPDM production
  - Modification of HOSO into gel form produces a more rigid material
- Peroxide-cured EPDM possesses much faster scorch times and vulcanization rates when compared to sulfur-cured EPDM
  - Use of antioxidants and coagents to slow rate had no effect
- Peroxide-cured EPDM with HOSO can improve the heat aging performance of the compound.
- Identify target part applications – includes body plugs, hoses, grommets

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Questions