

Comparative Study of Silica, Carbon Black and Novel Fillers in Tread Compounds

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ABSTRACT

In response to increasing demands for improved fuel economy and performance, companies are seeking advancements in tire technologies ranging from novel constructions to new material systems. Innovations and technology development of tire tread provide exciting opportunities to make strides in low rolling resistance tires.

The chemical formulation of tread compounds can significantly impact tire performance for key attributes including rolling resistance, traction and wear. In particular, fillers in elastomer compounds significantly affect the performance of tread compounds. Historically, carbon black was the primary filler in tread compounds and provided enhancement of the tread's wear resistance. Now, with the focus on low rolling resistance tires, emerging commercial options for fillers include new silicas as well as non-commercial, unique fillers with varied chemistries and surface geometries.

In this study, a variety of fillers were evaluated in a model tread compound for low rolling resistance tires. Material properties were compared for tread formulations using a range of compounding ingredients including carbon black, silica, dual phase carbon black-silica, silanol, and treated aramid fiber granules. Key findings include effect of fillers on cure kinetics, tensile properties, durometer and tear resistance.

Viscoelastic properties are correlated to on-vehicle performance for rolling resistance, traction and handling by assessing dynamic mechanical analysis predictors in various temperature regions. This study shows that selection of unique fillers can provide a promising alternative to standard carbon black and silica reinforcements, as indicated by dynamic mechanical analysis lab predictors, including reduction of tangent delta at 60°C to predict improved rolling resistance. The primary technical challenges and potential future opportunities for using novel fillers in tread compounds are also discussed.

INTRODUCTION

Fuel economy continues to be a leading factor influencing consumer vehicle purchases and has increased as a key driver for buying decisions within the past decade¹. While overall vehicle weight and powertrain systems have a significant impact on fuel economy, tires can provide opportunities for further improvements in vehicle fuel efficiency. As an estimate, reducing tire rolling resistance by ten percent can provide one to two percent improvement in fuel economy for passenger vehicles².

Within the past few decades, the technical tire community has developed many innovative solutions to contribute to improvements in automotive fuel efficiency. From novel tire constructions to new material systems, tire companies have provided new products to respond to the increasing demands for higher mileage gasoline vehicles. The technical community has researched opportunities for improving rolling resistance of the tires while maintaining the critical balance of the other facets of the "magic triangle": all season traction and wear.

One specific area of focus for research has been using new raw materials for tire tread. Tread formulations have a large impact on key tire performance attributes such as rolling resistance, traction and wear. Typically, either styrene butadiene rubber (SBR) or blends of SBR with polybutadiene or natural rubber, are compounded with processing oils, fillers, cross-linking agents and additives. Fillers are used in tread formulations to reinforce the elastomers and improve wear resistance, but these materials also contribute to energy dissipation in the compound. During the 1990's, widespread replacement of carbon black filler with silica filler in original equipment manufacturer's tires was pioneered as the "Green Tire Concept" by a major tire manufacturer. Use of this filler with silane coupling agents provided unique properties such that rolling resistance was lowered and wet traction improved without detriment to tread-life³.

To meet future demands for further advancements in low rolling resistance tires, innovations and technology development of tire tread provide an exciting opportunity to evaluate emerging filler options. Potential products include new silicas with varied surface areas, unique fillers with varied chemistries and surface geometries, as well as bio-based or recycled fillers.

In this study, we evaluated several key advanced fillers to assess their performance in high silica "green" tire tread formulations and standard, carbon black based tread compounds. Although these novel fillers have been examined individually in previous studies, this paper aims to provide a compilation study of fillers in comparable recipes. Fillers were selected based upon results presented in several technical papers, where either improvements in rolling resistance or other key performance attributes were noted. Material choices included carbon black, highly dispersible silica, hybrid of carbon black-silica, broad aggregate carbon black, silanol filler, butadiene rubber-acrylate terpolymer and treated aramid fiber granule.

The purpose of the study was to provide a direct comparison between emerging filler options and to evaluate key performance characteristics of the resulting tread compounds. A screening process was used to compare cure kinetics, unaged and aged physical properties as well as performance predictors using dynamic viscoelastic analysis of model tread formulations

containing advanced fillers. Based upon the results, an optimized formulation was compounded and evaluated using the same methodology.

EXPERIMENTAL

Fillers

Five unique fillers were selected for evaluation in two model tread compounds; one primarily silica filled and the other carbon black filled, as shown in Table I. The study was conducted so that the novel fillers are compared directly with their respective control fillers, rather than comparing properties between the two sets of rubber compounds. These experimental fillers were identified based upon previous reports of their enhancement to at least one aspect of the magic triangle: rolling resistance, traction or wear. The trade names of the silica and carbon black fillers as well as the five novel fillers are detailed in the table below. In this study, the nomenclature of "silica," "silanol filler" and "BR-acrylate terpolymer" will be used to describe the fillers in the silica-based tread compounds. "Carbon black," "treaded aramid fiber granule," "hybrid CB-silica" and "broad-aggregate CB" will be the terms used for the carbon black-based tread formulations.

Table 1: Summary of Advanced Fillers Used in Formulations

Purpose	Filler Type	Base Compound	Tradename	Supplier
Control	Silica	Silica	Ultrasil [®] 7000 GR	Evonik Industries
Experimental	Silanol Filler	Silica	SO1458 trisilanolphenyl POSS [®]	Hybrid Plastics
Experimental	BR-Acrylate Terpolymer	Silica	Nanoprene [®] B M750H VP RW	Lanxess
Control	Carbon Black (CB)	Carbon Black	N234 Carbon Black	Cabot Corporation
Experimental	Treated Aramid Fiber Granule	Carbon Black	Sulfron [®] 3001	Teijin
Experimental	Hybrid CB-Silica	Carbon Black	CRX [™] 4210A Dual Phase Filler	Cabot Corporation
Experimental	Broad Aggregate CB	Carbon Black	Vulcan [®] 1436 Broad Aggregate Size CB	Cabot Corporation

Highly dispersible, amorphous precipitated silica is commonly used as reinforcing filler in conjunction with a bifunctional organosilane coupling agent in energy-efficient tire tread. The surface area of the precipitated silica is often measured by the adsorption of nitrogen molecules onto the silica, as described in the Brunauer, Emmett, and Teller (BET) theory⁴. Silicas with high BET surface area are desirable in achieving low rolling resistance because of their improved reinforcement and large interfacial area, which provides more areas for bonding with the polymer with the aid of the coupling agent. Highly dispersible, reinforcing silica with BET surface area of 170 m²/g was selected as the control filler for the silica compound due to its prevalence in low rolling resistance tire tread formulations. Two fillers were chosen as a

comparison to highly dispersible silica filler technology, due to their compatibility with this type of formulation chemistry: silanol filler and butadiene rubber-acrylate terpolymer (BR-acrylate terpolymer), described in Table 1.

The first experimental filler in the silica compound was polyhedral oligomeric silsesquioxane (POSS), a member of the silanol chemical family. For this study, trisilanolphenyl filler with chemical formula $C_{42}H_{38}O_{12}Si_7$ was chosen. Organic phenyl groups are attached at the corners of the cubic inorganic silsesquioxane cage, which has three active silanol functional groups. Potentially, the cubic nature of the POSS together with its silanol functional groups could provide unique nano-reinforcement of the silica tread compound⁵. In published literature, POSS has been shown to increase $\tan \delta$ at 0°C , which would predict better wet traction without increasing $\tan \delta$ at 60°C , predicting no change in rolling resistance⁶. Use of this filler has been shown to improve DIN abrasion resistance and tread-life. Figure 1 shows the cage-like POSS chemical structure which contains both organic and inorganic regions.

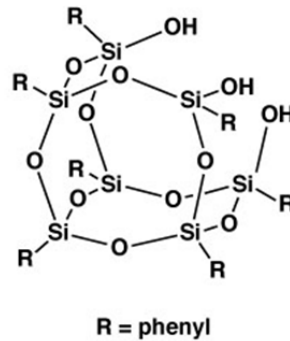


Figure 1: Chemical structure of trisilanolphenyl silsesquioxane (silanol filler)⁷

The second filler, BR-acrylate terpolymer, contains nano-scale spherical particles approximately 50nm in diameter of cross-linked butadiene rubber with an outer coating of hydroxyl groups, providing a hydroxyl content of 30%. The hydroxyl functionalization of the terpolymer can facilitate better interaction between the rubber matrix and the polar silica filler⁸. As a result of more silica/polymer bonding, the attraction between silica aggregates will be reduced, leading to lower Payne effect and better silica dispersion. A terpolymer with a T_g of -75°C was chosen to be compatible with the T_g of the other polymers in this study. When used as an additive, the nano-terpolymer can enable lower rolling resistance, increased dry traction, improved handling through increased stiffness, and improved abrasion resistance, leading to longer tread-life⁹.

Carbon black type N234 was chosen as the second control filler due to its prevalence in the market. With its small particle size, large surface area and high structure, N234 is a common choice for low rolling resistance tire tread compounds. The high surface area provides more interfacial area to interact with the polymer chains. Experimental fillers in the carbon black based formulations include treated aramid fiber granule, a hybrid of carbon black-silica, and broad aggregate carbon black.

The aramid fiber granule compounding ingredient is surface treated with peroxide to create radicals that interact with the carbon black surfaces during mixing. Through reaction with the carbon black particles, the treated aramid fiber granule may reduce filler-filler interactions which decrease the Payne effect, as determined by the modulus at low strains. The lower Payne effect can result in lower hysteresis and better fuel economy and tread-life. The manufacturer also reports a reduction in tread cuts, chipping and chunking with use of this product. Figure 2 shows the chemical structure of the base para-aramid fiber that is then chemically modified to reduce filler-filler interaction.

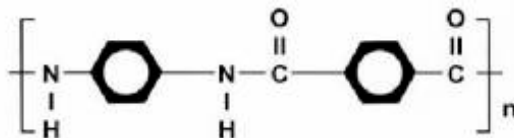


Figure 2: The aramid fiber granule is based on chemically modified para-aramid fiber (poly(paraphenylene terephthalamide))¹⁰

The carbon black-silica dual phase filler has particle morphology similar to that of carbon black, but contains both silica and carbon black moieties, grafted together in a flame process¹¹. By incorporating both silica and carbon black domains into the same particle, the filler-filler network is reduced. In this filler, the carbon black is grafted with 10% silica by weight, which provides benefit to hysteresis without detriment to abrasion resistance. Compounds with the carbon black-silica dual phase filler may exhibit lower filler-filler interaction, as evidenced by lower Payne effect which will result in lower hysteresis and better fuel economy. The compounds may also show higher bound rubber formation, which would indicate better polymer-filler interaction which could lead to better tread-wear¹².

Broad aggregate carbon black filler was also investigated as filler in the carbon black tread compound. Overall, the broad aggregate carbon black has a specific surface area approximately midway between that of N375 and N220, yet the filler particles of different aggregate sizes are not able to pack as closely together as filler particles of uniform size and therefore have a larger average spacing between particles¹¹. In the rubber system, the inter-particle spaces allow the polymer chains access to the filler surface, resulting in less filler-filler interaction and hence, less hysteresis. In addition, carbon black with a broad particle size distribution has been shown to provide higher abrasion resistance, leading to longer tread-life.

Figure 3 shows photographs of the key novel fillers used throughout the study. The silanol filler and the BR-acrylate terpolymer were used in the silica-filled tread recipe, while the treated

aramid fiber granule, hybrid CB-silica and broad aggregate carbon black were used in the carbon black-filled recipe.

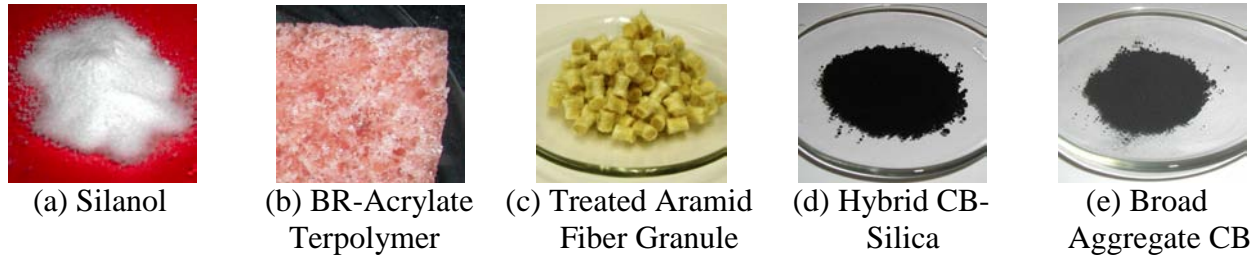


Figure 3: Photographs of novel fillers.

Materials

A model tire tread formulation of solution styrene-butadiene rubber (S-SBR) and solution polybutadiene (S-BR) was used as the basis for this comparative filler study. Table 2 provides an overview of the key chemical ingredients used in the two sets of experiments: carbon black formulation and silica formulation. Formulations were developed to target a compound durometer range of 60-65 Shore A hardness.

Table 2: Recipe Formulation (parts per hundred rubber, by weight)

Formulation		
Component	Silica Formulation (phr)	Carbon Black Formulation (phr)
Solution SBR (oil extended)	103.12	103.12
Polybutadiene Rubber	25.0	25.0
N234 Carbon Black	15.0	75
Highly Dispersible Silica	65.0	0
Silane Coupling Agent	5.2	0
TDAE Processing Oil	10	10
Zinc Oxide	2.5	2.5
Microcrystalline Wax	2.0	2.0
Antidegradant	2.0	2.0
Antidegradant	0.5	0.5
Stearic Acid	2.0	2.0
Process Aid	2.0	2.0
Sulfur	2.0	2.0
Sulfenamide Accelerator	1.7	1.7
Guanidine Accelerator	2.0	2.0
Total phr	240.02	229.82

The elastomers used in this study include Buna VSL 5025-2, an S-SBR with Mooney viscosity of 47 (ML(1+4)100°C=47) with 50% vinyl and 25% styrene content supplied by Lanxess, and Budene 1207, a solution high cis (cis-1,4 content =98%) polybutadiene, which was supplied by Goodyear Chemical. The S-SBR is oil-extended with treated distillate aromatic extract (TDAE) at 37.5 phr and has a glass transition temperature of -29°C. Additional ingredients include a combination of highly dispersible precipitated silica and a bifunctional polysulfide organosilane coupling agent, and type N234 carbon black. Other chemicals typical of tread formulations such as sulfur, accelerators, wax, processing oil and zinc oxide are used in typical proportions.

The five fillers examined in this study used the reference recipe formulations described above. In the silica control compound, 65 phr (parts per hundred rubber) silica filler is used in combination with 15 phr carbon black. Additional filler loading of 3.5 phr silanol filler and 10 phr BR-acrylate terpolymer were used in the experimental silica-based compounds, respectively.

The second set of experiments was based upon the model carbon black formulation. Treated aramid fiber granule was added at loading level of 2 phr in addition to the 75 phr carbon black. For the hybrid CB-silica and broad aggregate CB formulations, all 75 phr of N234 carbon black was replaced. The hybrid CB-silica recipe required the addition of 2.7 phr silane coupling agent in order to effectively couple the filler to the rubber matrix. Detailed formulation information is provided in Appendix A for all seven compounds.

Processing

The two sets of model tire tread formulations were compounded in a Farrel Model 2.6 BR Banbury Mixer using a 70% fill factor with ram pressure set to 40 psi. A three stage mixing process was used, as outlined in Table 3, in which elastomers, fillers, processing oil, silane coupling agent (where applicable), microcrystalline wax, antidegradants, zinc oxide, stearic acid and the processing aid were added in the first pass. In the first two mixing stages, the rotor speed was increased after the ingredients were incorporated in order to bring the batch temperature to 160°C to complete the silanization reaction. The primary and secondary accelerators and sulfur were mixed with the masterbatch in the final (productive) pass.

All tread compounds followed the outlined procedure, with the exception of the silanol filler. This novel filler was added during the second stage of mixing in order to minimize contact with the acidic precipitated silica during mixing. The acidic nature of the silica can destroy the free radicals on the surface of the silanol filler and render the filler less reactive.

The rubber was sheeted out on a Farrel two-roll mill after each Banbury mixing stage. Cure rate information was determined according to ASTM D 2084 using an oscillating disc rheometer (Tech Pro rheoTech ODR, 3° arc)¹³. Rubber samples were compression molded with curing temperature equal to 160°C and molding time equal to $t_{90}+5$ minutes. Processing properties including Mooney viscosity, ML(1+4) at 100°C, were determined according to ASTM D 1646 in a Monsanto MV 2000 Viscometer, using the large rotor¹⁴.

Table 3: Mixing Protocol of Tread Compounds

Mixing Procedure		
<i>Silica Formulation Mix Sequence</i>	<i>Carbon Black Formulation Mix Sequence</i>	<i>Time</i>
Stage 1	Stage 1	
Elastomers	Elastomers	0'
2/3 silica + coupling agent	2/3 carbon black	1'
1/3 silica + carbon black + processing oil + other ingredients	1/3 carbon black + processing oil + other ingredients	2'
Sweep	Sweep	3'
Adjust rotor speed to hold at 160-165°C	Adjust rotor speed to hold at 160-165°C	3.5' – 8'
Dump	Dump	Hold 2' at 160-165°C (total mix time = 10')
Stage 2	Stage 2	
Masterbatch	Masterbatch	0'
Add silanol filler, if applicable		1'
Increase rotor speed to hold at 140-145°C	Increase rotor speed to hold at 140-145°C	1.5'
Dump	Dump	Hold 4' at 140-145°C
Stage 3 (productive)	Stage 3 (productive)	
1/3 masterbatch	1/3 masterbatch	0'
Sulfur + accelerators + 2/3 masterbatch	Sulfur + accelerators + 2/3 masterbatch	30"
Sweep	Sweep	1'
Dump	Dump	110°C or 2.5'

Physical Properties

Physical properties of the tread compounds were assessed for tensile strength, elongation, tear resistance and durometer. Tensile properties were tested according to ASTM D 412, Test Method A, Die C¹⁵. Five dumbbell-shaped tensile specimens per sample were die-cut from a 2-mm thick test plaque using a hydraulic die press. Tensile properties were evaluated using an Instron dual column testing system equipped with a 5-kN load cell and a long-travel extensometer. Gage length was 25mm and grip separation velocity was 500 mm/min. Shore A durometer was measured as directed in ASTM D 2240¹⁶. Peel tear strength at 100°C was assessed according to ASTM D413 and rebound resistance was determined as directed in DIN 53512^{17,18}.

Five tensile, tear and durometer specimens from each formulation were conditioned in an air oven at 70°C for 504 hours according to ASTM D 573¹⁹. After being removed from the oven, the specimens were conditioned overnight at room temperature on a flat surface. The heat aged properties, including tensile strength, modulus, ultimate elongation and Shore A hardness, were compared to the properties of the original specimens. Tested samples were 1mm in thickness instead of 2mm as specified in ASTM D 573 test method in order to maximize the oxygenation aging of the compound.

Viscoelastic properties were examined using dynamic mechanical analysis (DMA). Storage modulus (E'), loss modulus (E''), complex modulus (E*) and tan δ data were obtained through temperature sweeps in tension with frequency equal to 2 Hz using a Metravib 1dB machine.

RESULTS AND DISCUSSION

Throughout the results and discussion section, compounds using silanol and BR-acrylate terpolymer are compared directly to those using the control silica filler. Similarly, N234 carbon black filler is used as a control for the treated aramid fiber granule, hybrid carbon black-silica, and broad aggregate carbon black fillers. While results of all seven compounds are shown within each figure, it should be noted that formulation adjustments were made with the silica versus carbon black based control sets. For simplicity, cure package systems used within the silica based rubber and carbon black based rubber were not modified between the set of experiments. In further studies, it is recommended to optimize the accelerator to sulfur ratio in carbon black based compounds to control scorch time and crosslink density. Compounds were compared using a three tier approach: processing parameters, physical properties and tire performance attribute predictors.

Processing Parameters

Evaluation of key processing parameters provides information about required manufacturing times and constraints. Tread compounds using seven different filler options were evaluated for Mooney viscosity, scorch time and cure kinetics and compared to one another.

Mooney viscosity at 100°C is used to indicate the ease of processing tread compounds through an extruder, in which lower values are usually preferred. Figure 4 provides a comparison of the effect of filler type to the resulting viscosity. In the silica based formulations, the silanol filler

compound had a lower viscosity than the control compound, while the BR-acrylate terpolymer exhibited significantly higher viscosity than its comparator fillers. For the carbon black based formulations, the treated aramid fiber granule compounds had a slightly lower viscosity than the control. Both the hybrid carbon black-silica and broad aggregate carbon black compounds had increased viscosities compared to standard carbon black.

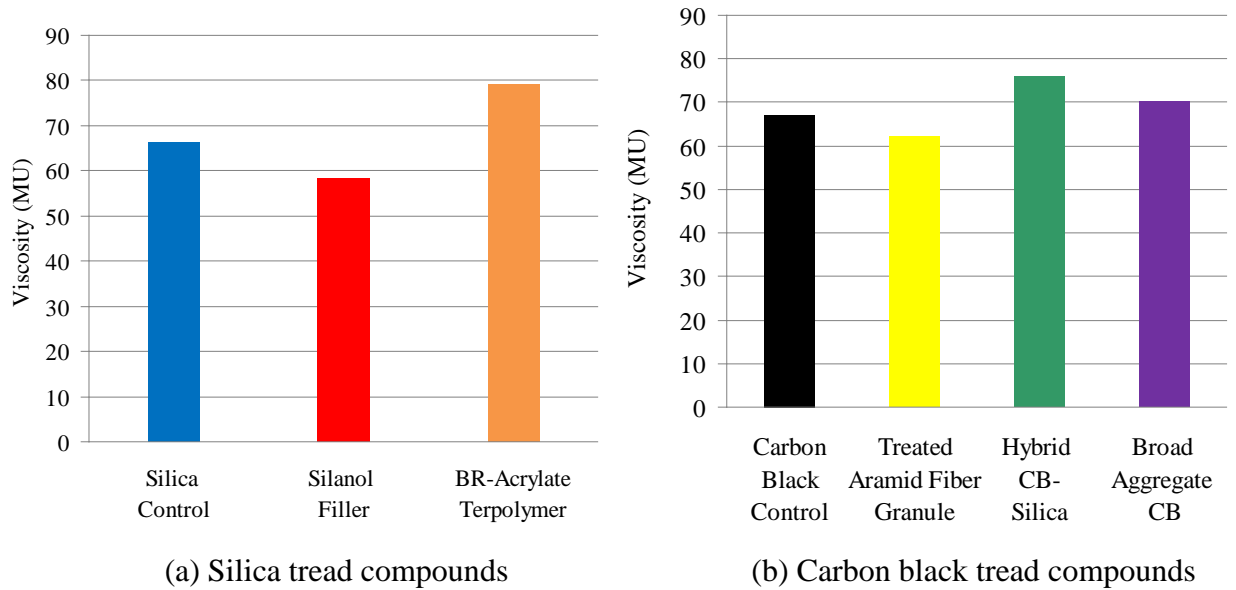


Figure 4: Mooney viscosity at 100°C for tread compounds using different fillers.

As shown in Figure 5, the carbon black based formulations generally had shorter t_{s2} scorch times than the silica based formulations. The hybrid CB-silica compound exhibited longer t_{s2} scorch time relative to the carbon black control due to acidic nature of the silica portion of filler which tends to retard cure and increase scorch safety. Longer scorch times are desirable for ensuring processing safety during manufacturing.

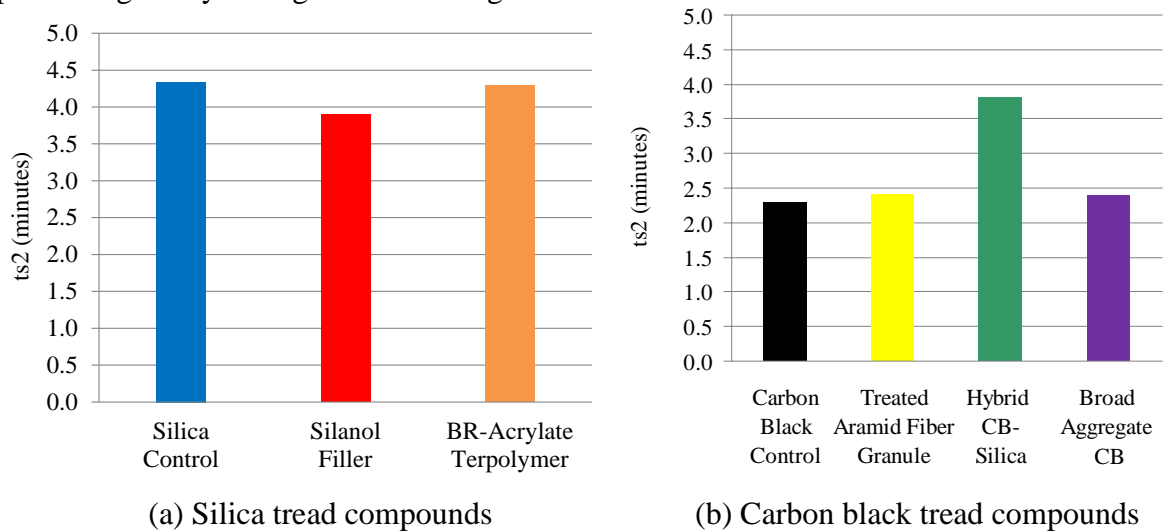


Figure 5: Scorch time (t_{s2}) of rubber during curing with ODR rheometer.

In addition to Mooney viscosity and ODR t_{s2} scorch times, the ODR rheometer was used to characterize the cure time of the novel filler tread compounds. Figure 6 compares cure times of the rubber at 90% maximum torque, t_{c90} at 160°C. The processing results indicated that the silanol filler had a shorter cure time than the silica control compound. Compounds with the hybrid carbon black-silica filler had a longer cure time than the other carbon black based samples and had similar cure parameters to those of the silica control samples. Overall, the fillers used in carbon black based compounds had significantly lower cure times than the silica based compounds.

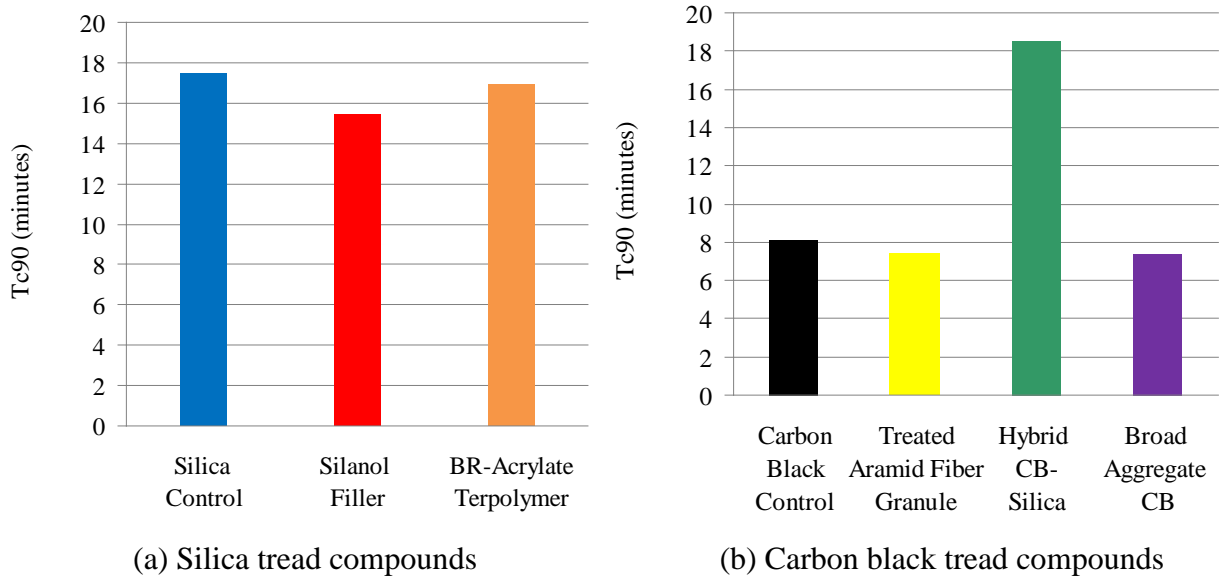
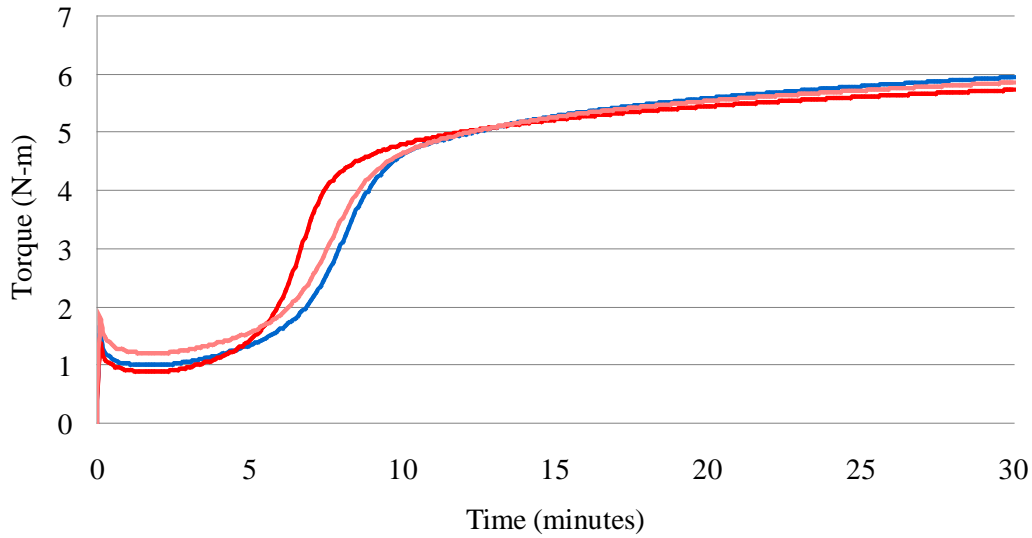


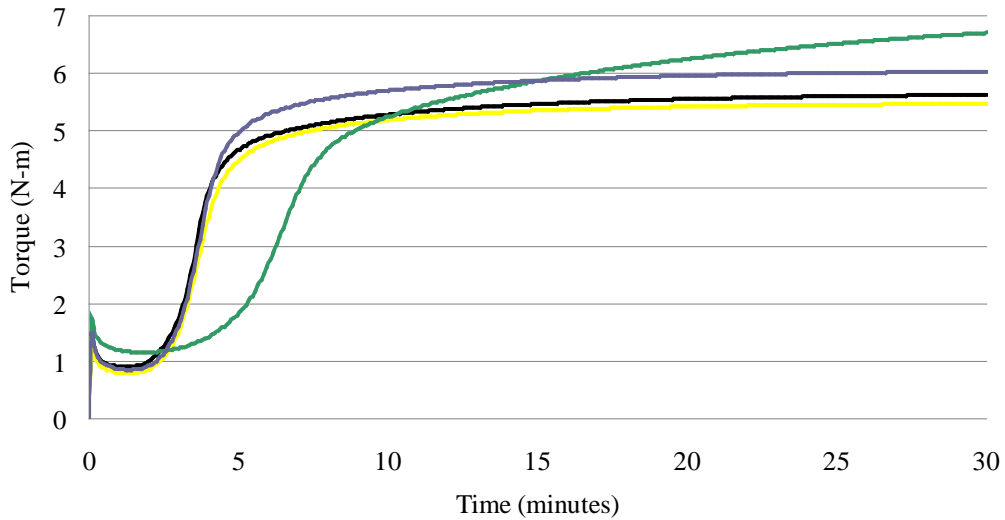
Figure 6: T_{c90} (time to 90% cure) of rubber during curing with ODR rheometer.

Evaluation of the measured torque during rubber curing provides insight into the state of cure and processing windows. As shown in Figure 7, the measured torque during cure at 160°C for the seven compounds indicates that the silica compounds had longer scorch times but slower rate of cure than the carbon black compounds. While the hybrid carbon black-silica compound is formulated with carbon black as its primary filler, this rubber exhibited a rheometry curve closely aligned with that of silica based compounds. Both the hybrid carbon black-silica compound and broad aggregate carbon black silica compounds had higher maximum torques, or state of cure, than the other compounds.



— Silica Control — Silanol Filler — BR-Acrylate Terpolymer

(a) Silica tread compounds



— Carbon Black Control — Treated Aramid Fiber Granule — Hybrid CB-Silica — Broad Aggregate CB

(b) Carbon black tread compounds

Figure 7: Measured rheometer torque for curing rubber at 160°C.

Physical Properties

In addition to evaluating processing parameters, key physical properties were assessed for each of the seven compounds, including durometer and tensile properties. Figure 8 shows the affect of filler on rubber hardness, as measured with Shore A durometer. Compared with the silica control sample, addition of the silanol filler reduced the hardness of the rubber whereas the BR-

acrylate terpolymer filler had no effect on the durometer. For the carbon black based compounds, the addition of hybrid carbon black-silica filler decreased the durometer whereas increases were noted for the treated aramid fiber granule and broad aggregate carbon black filler compounds.

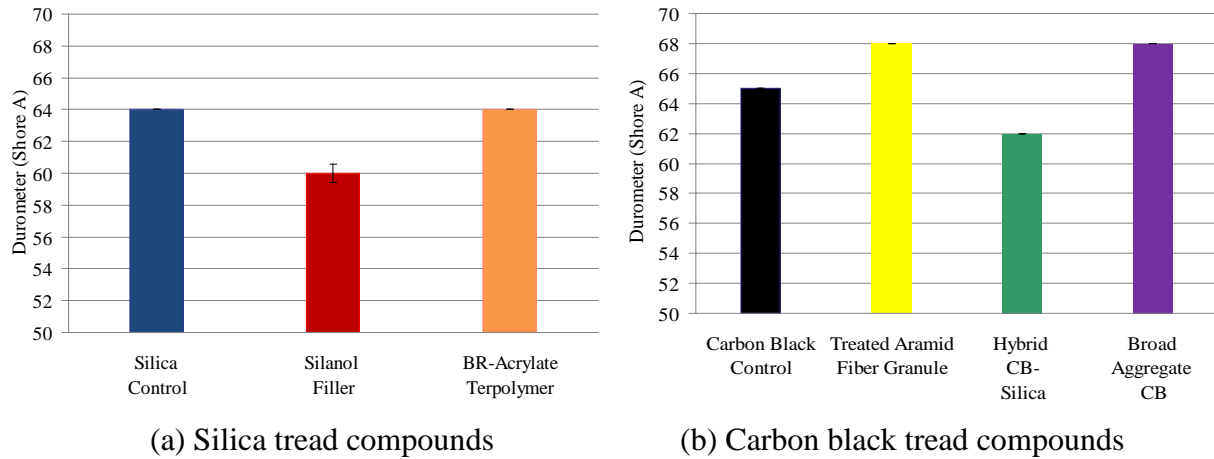


Figure 8: Hardness measurement (Shore A durometer) of as-molded rubber.

Tensile properties were evaluated for the novel filler compounds, including tensile strength, percent elongation at break, modulus at 100% elongation and modulus at 300% elongation, shown in Figures 9-12, respectively. Compounds using hybrid carbon black-silica filler showed a decrease in tensile strength to 12MPa compared to the carbon black control at 16MPa. The other novel fillers exhibited similar tensile strength compared to the control compounds, as shown in Figure 9.

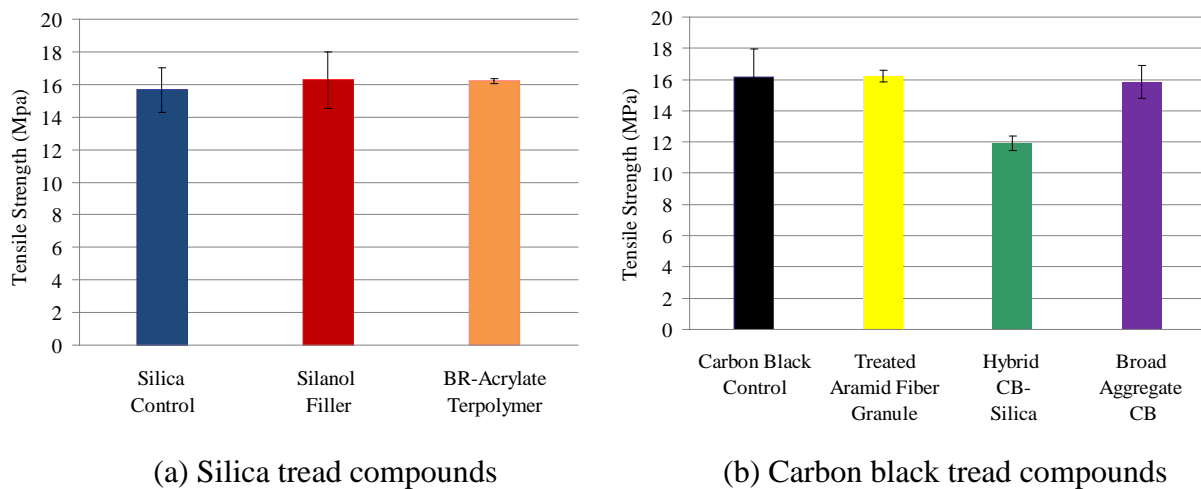


Figure 9: Tensile strength of as-molded rubber samples using various fillers.

As noted in Figure 10, percent elongation at break was slightly improved for the silanol and BR-acrylate terpolymer compounds compared to the silica control sample. For the carbon black based samples, the addition of specialty fillers caused a reduction in elongation values by 10-20%. Comparison of tensile modulus at 100% elongation in Figure 11 indicated that usage of

novel fillers increased values for carbon black based formulations relative to the carbon black control, whereas the different fillers decreased moduli for the silica based subset of materials relative to the silica based control compound. Similarly, in Figure 12, aramid fiber granule filler and broad aggregate carbon black filler increased moduli at 300% elongation.

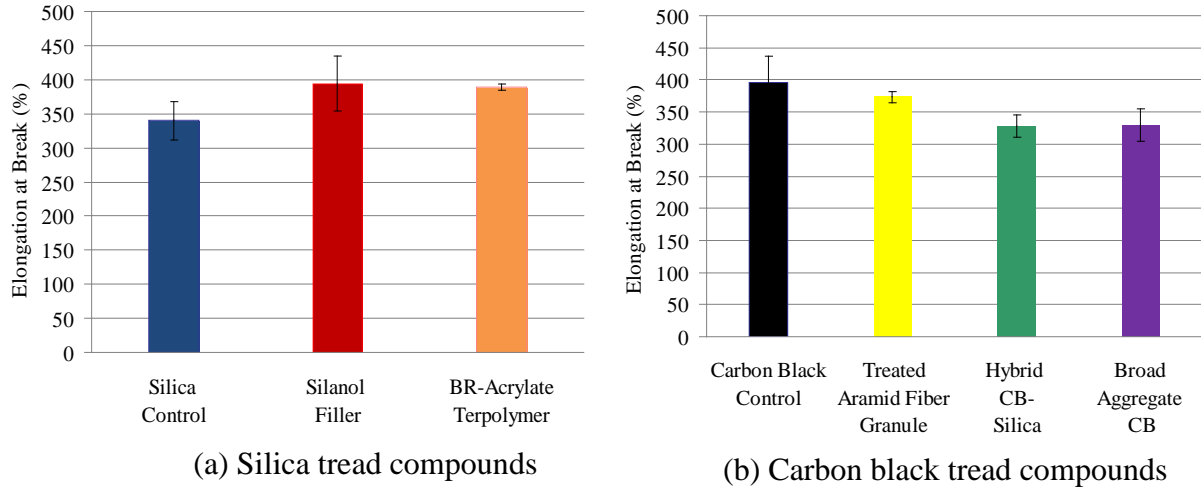


Figure 10: Elongation at break of as-molded rubber using various fillers.

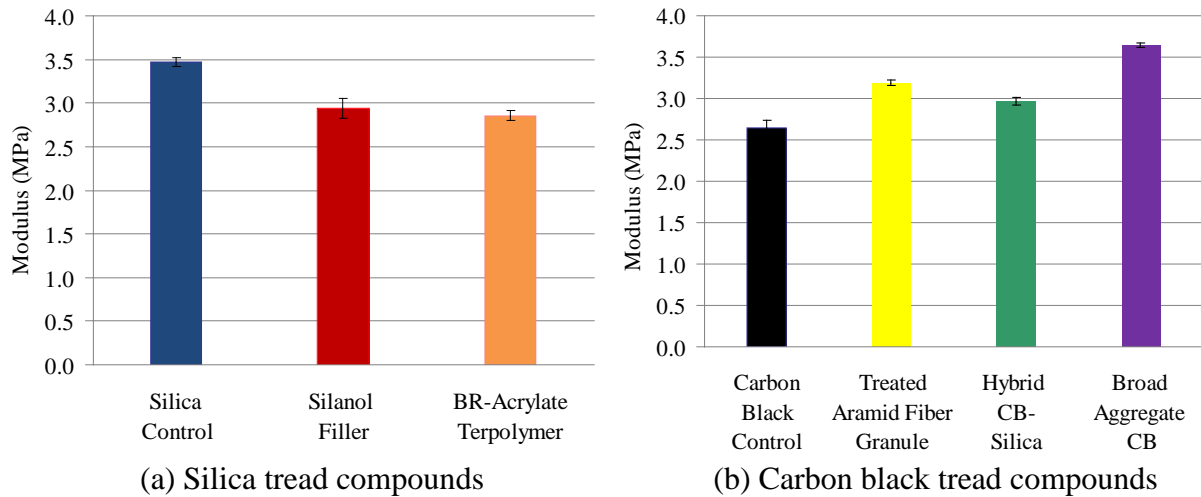
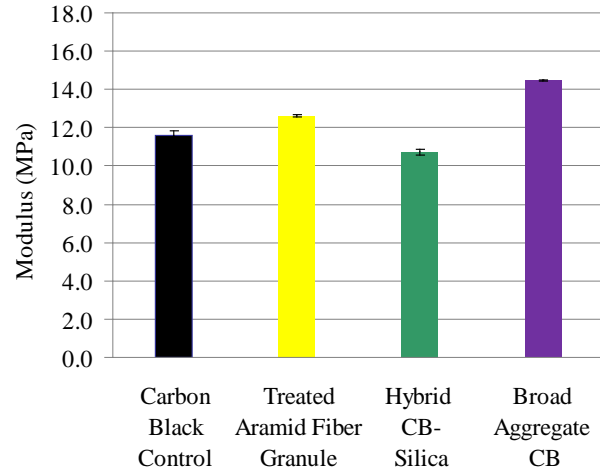
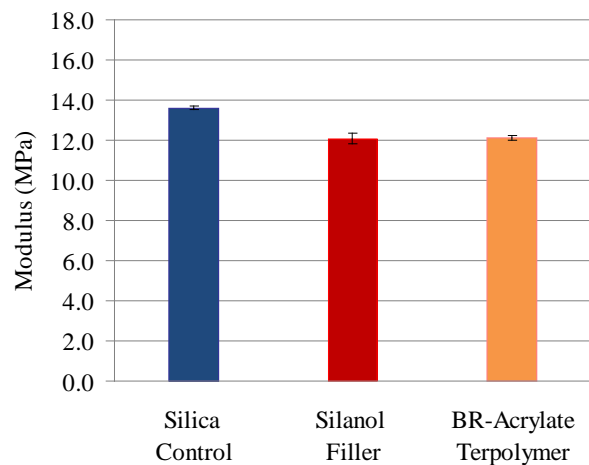


Figure 11: Modulus at 100% elongation for as-molded samples using various fillers.



(a) Silica tread compounds

(b) Carbon black tread compounds

Figure 12: Modulus at 300% elongation for as-molded rubber samples using various fillers.

Rubber samples were assessed for aged physical properties by conditioning samples at 70°C for seven days prior to testing. Table 4 provides a summary of the aged physical results for each of the sets of experiments. Tread compounds with novel fillers exhibited similar changes in hardness as the control samples. The compound using BR-acrylate terpolymer showed a noticeable change in aged tensile properties, as compared to the silica control sample.

Table 4: Aged Physical Properties of Novel Fillers in Rubber

Heat Aged Test	Silica Control	Silanol Filler	BR-Acrylate Terpolymer	Carbon Black Control	Treated Aramid Fiber Granule	Hybrid CB-Silica	Broad Aggregate CB
Shore A Durometer Change (points)	8	8	7	10	8	11	7
Tensile Strength Change (%)	-1.8	0.1	-7.3	-7.9	-7.0	18.8	-2.9
Elongation Change (%)	-11.1	-8.2	-24.8	-24.5	-16.0	-15.5	-19.9
100% Modulus Change (%)	-3.4	-5.6	-39.0	-49.3	-8.2	-32.1	-23.7
300% Modulus Change (%)	10.2	10.8	29.5	29.3	12.5	N/A	N/A

Tire Performance Predictors

Dynamic mechanical analysis (DMA) is often utilized as a laboratory predictor for performance of tread compounds under different environmental conditions. Previous literature has shown that obtaining the storage modulus, E' , at -20°C in tension provides a predictive measurement of winter traction of tread compounds²⁰. As shown in Figure 13, all samples using novel fillers showed an equivalent or lower value of E' at -20°C compared to the control samples, indicating equal or better winter traction performance. In particular, the hybrid of carbon black-silica showed the most significant improvement compared to the carbon black control sample.

Compounds using the BR-acrylate terpolymer filler are predicted to have improved winter traction performance relative to the silica control, based upon this laboratory test.

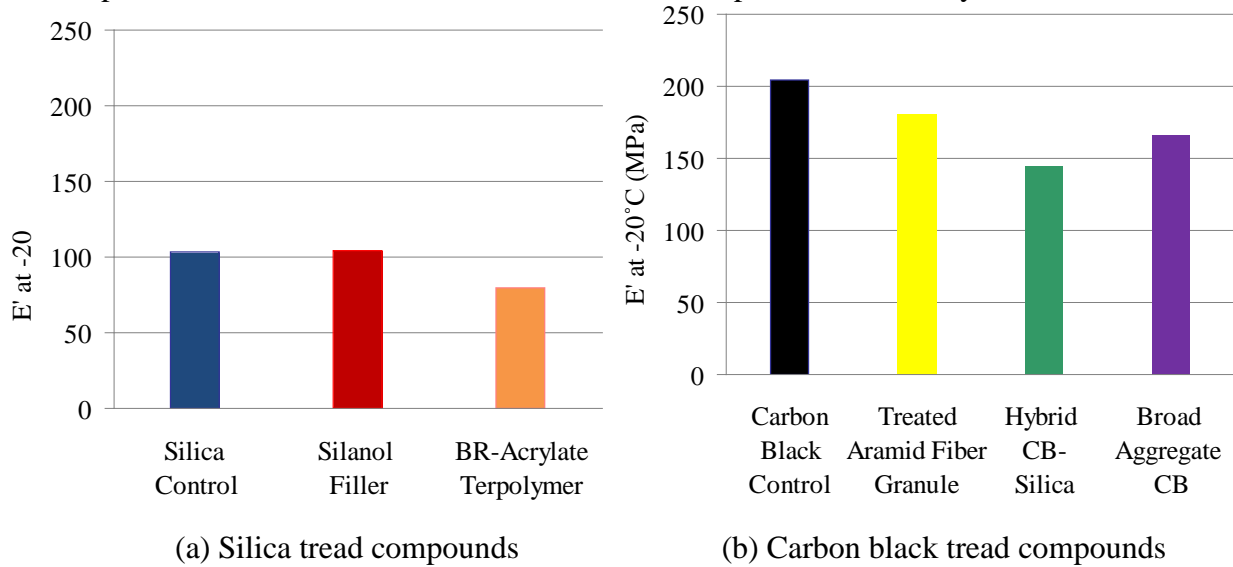


Figure 13: Storage modulus, E' , at -20°C in tension, as a predictor for winter traction (lower is better).

In order to assess the performance of tread compounds for ice traction, tangent delta at -10°C is used as a predictive tool, where higher values are preferred. Tangent delta is the ratio of loss modulus to storage modulus at a given temperature and frequency. Figure 14 compares the predicted ice traction performance for the seven different tread compounds. Compounds using hybrid carbon black-silica had the largest improvement compared to the carbon black control rubber. Silanol filler based compounds also showed a significant improvement compared to the silica control sample. Results of the test indicate that the other novel fillers would have either similar or slight improvement in ice traction compared to the control tread.

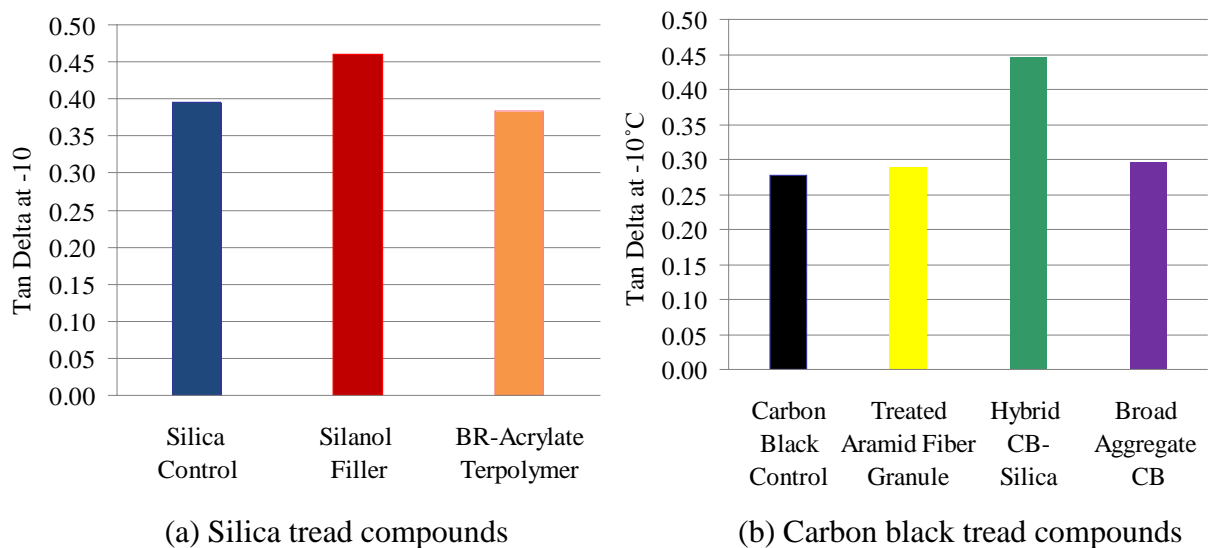


Figure 14: Tangent delta at -10°C in tension, as a predictor for ice traction (higher is better).

Figure 15 predicts the performance for wet traction by comparing tangent delta values at 0°C in tension, where higher values are preferred. With the exception of BR-acrylate terpolymer, all compounds using novel fillers showed an improvement in wet traction predictors compared to the base control compounds. Compounds using silanol filler and hybrid carbon black-silica were noted for their significant improvement over the control values.

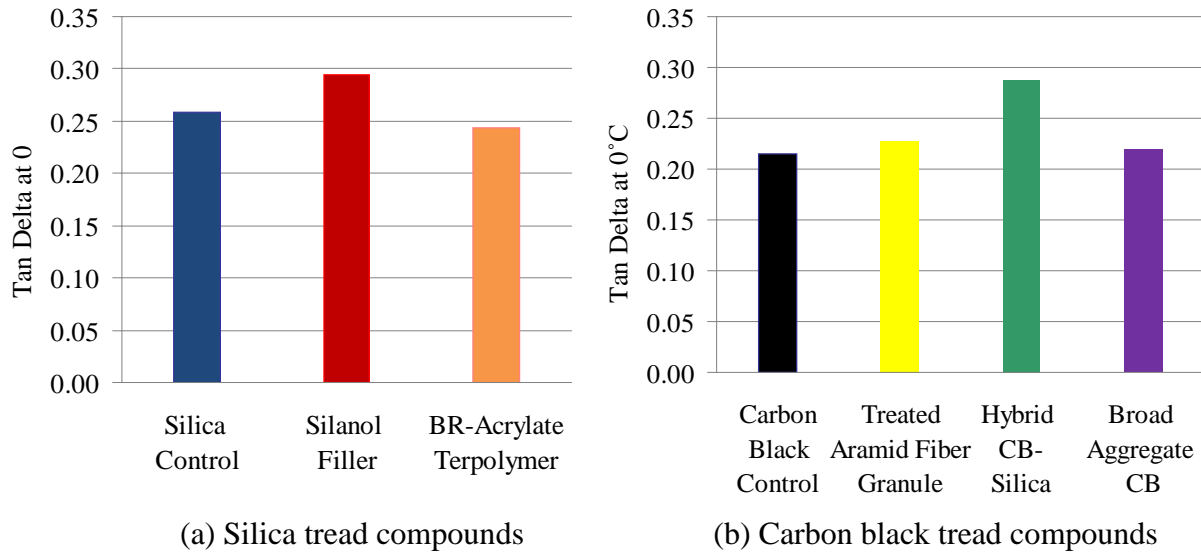


Figure 15: Tangent delta at 0°C in tension, as a predictor for wet traction (higher is better).

Similarly, tangent delta values at 60°C are used as a predictive tool for rolling resistance of tread compounds. In this case, lower tangent delta values at this temperature correlate to lower rolling resistance in tires²¹. The BR-acrylate filler, hybrid carbon black-silica filler and broad aggregate carbon black filler had tangent delta values at 60°C that were lower than their corresponding control samples, thus predicting improved rolling resistance. Based upon the results in Figure 16, silanol filler and treated aramid fiber granule compounds had similar rolling resistance to the silica control and carbon black control tread rubber, respectively.

In addition to the results presented here, Zwick rebound was also evaluated for each of the tread compounds. Results were consistent with the tangent delta predictions, in which the carbon black based compounds had lower rebound than the silica based compounds. The hybrid carbon black-silica compound showed higher rebound than its corresponding carbon black control.

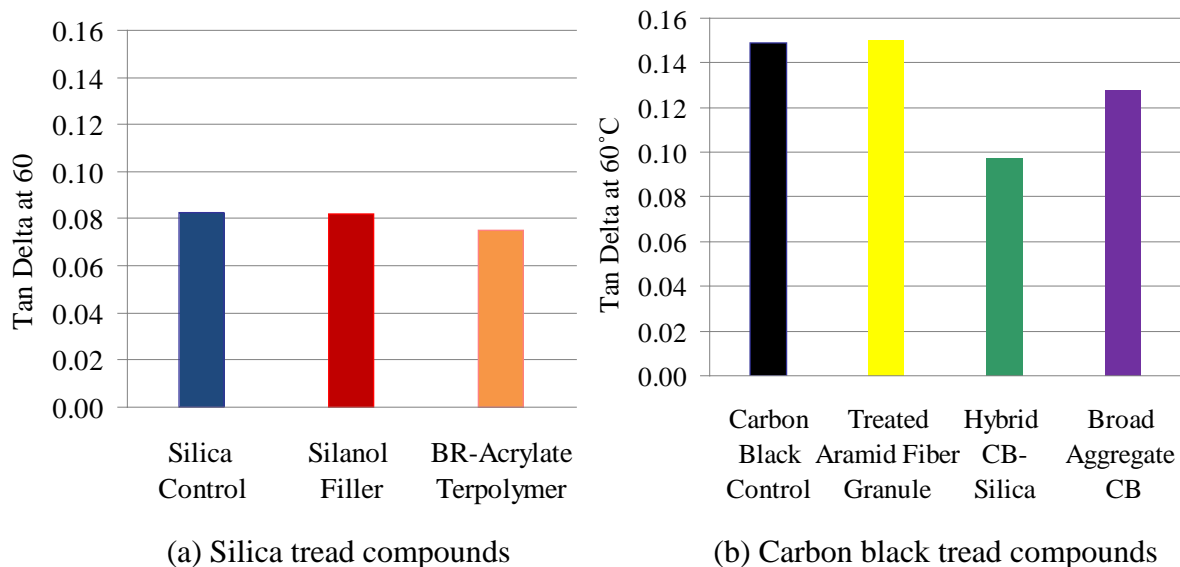


Figure 16: Tan delta at 60°C in tension, as a predictor for rolling resistance (lower is better).

Dynamic mechanical analysis can provide a useful tool to evaluate, compare and predict tire performance predictors of tread compounds. In the radar plots in Figure 17 and 18, the novel fillers are compared directly to each of their respective control fillers: silica and carbon black. In Figure 17, the overall performance of silanol filler compounds and BR-acrylate terpolymer is normalized according to the silica control values and presented so larger numbers are favorable to each of the attributes. Several trade-offs are apparent between the predictors for dry handling and traction. While both alternative fillers showed reduction in dry handling performance predictors, fuel economy was favorable for the BR-acrylate terpolymer and wet traction was favorable for the silanol filler. Overall, these unique fillers exhibited promise for future development based upon the predictions for fuel economy and wet traction.

In Figure 18, the carbon black based formulations are normalized to the values of the control sample for a comparison of winter traction, ice traction, wet traction, dry handling and fuel economy based upon DMA laboratory predictors. The broad aggregate carbon black showed improvement in fuel economy prediction while maintaining most of the other key performance attributes. The distribution of carbon black particle sizes most likely provided greater spacing between the filler particles, which would result in less filler-filler interactions and hence, less hysteresis due to the Payne effect. Compounds using hybrid carbon black-silica exhibited significant improvements in fuel economy and traction while predicting lower dry handling performance using this particular formulation.

It is important to note that the DMA testing was performed in tension mode at low strain (0.2%) for the studies presented in this paper. Using higher strains in tension mode, or other testing geometry configurations, including compression and shear deformation modes, may yield different results. In the case of the treated aramid fiber granules, tan delta at 60°C was similar to the control carbon black compound when using tension deformation mode. As discussed in the Fillers section of this paper, previous literature reports that adding the treated aramid fiber granules as a compounding ingredient can have a synergistic effect with the carbon black to

reduce rolling resistance of tires by lowering the Payne Effect and thereby reducing hysteresis. While the improvement in rolling resistance was not observed in this particular study, the wet traction DMA predictor indicated that use of treated aramid fiber granules may offer benefits for this attribute.

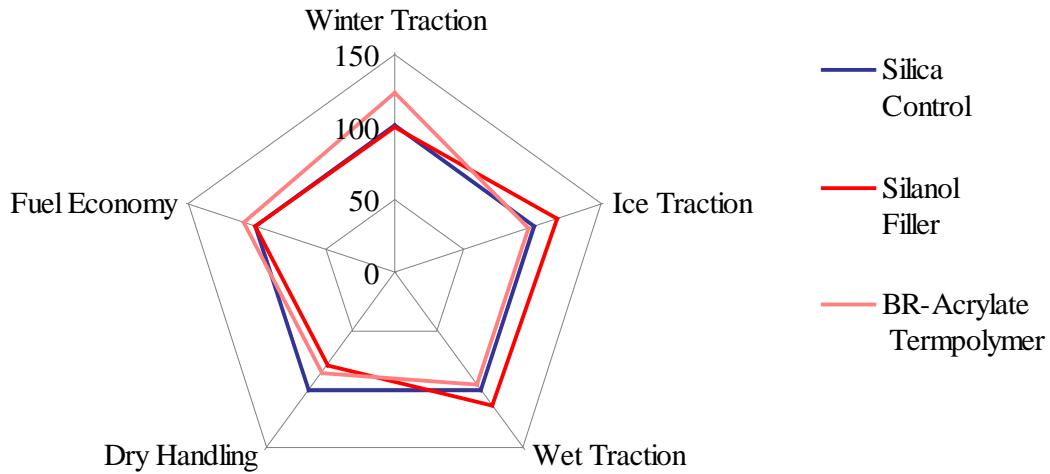


Figure 17: Normalized DMA performance predictors of novel fillers compared to silica control compound.

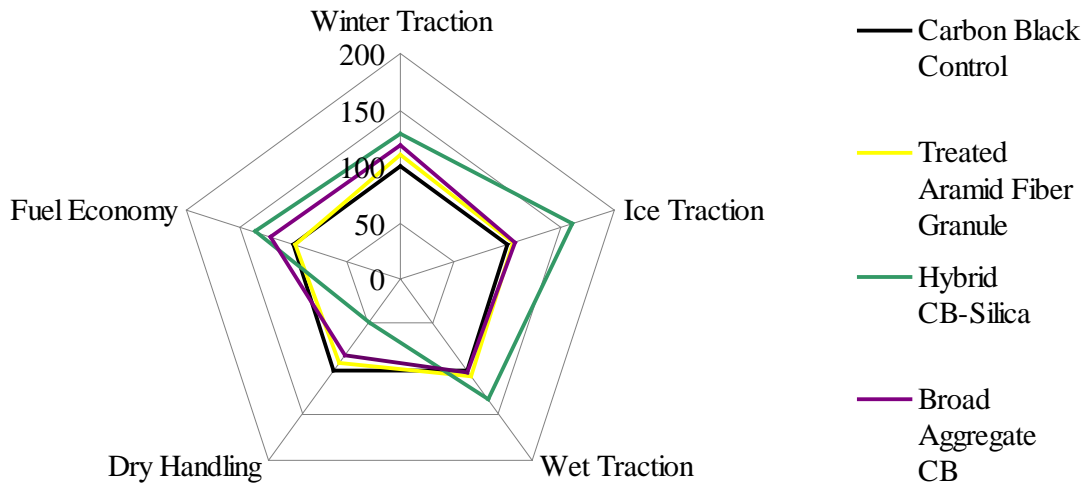


Figure 18: Normalized DMA performance predictors of novel fillers compared to carbon black control compound.

Formulation Optimization

Upon completion of the silica and carbon black novel fillers investigation, an optimization study was undertaken to determine if further improvements in rolling resistance could be obtained by combining promising novel fillers with other proven technologies. An optimized formulation

was developed that is representative of the best-available technology for low-rolling resistance tire tread compounds and incorporates promising features of the specialty tread formulations described earlier in this study. The intention of this phase was to further enhance a low rolling resistance tire recipe by combining one of the alternative fillers with other advanced silica, oil and elastomer technologies.

The formulation for the control compound in the optimization study utilized a tin-coupled, amine modified solution SBR, DOW SLR-4602. According to the supplier, this backbone- and chain-end modified polymer exhibits improved rolling resistance as indicated by lower hysteresis ($\tan \delta$ at 60°C), improved abrasion resistance and better ice traction ($\tan \delta$ at -10°C)²². Based on previous research, this functionalized polymer displays an affinity for both carbon black and silica fillers and was chosen as the control SBR polymer due to its ability to lower the hysteresis of the tread compound, as measured by $\tan \delta$ at 60°C ²³.

Highly dispersible precipitated silica, Perkasil SM 660 from Grace Davison, with BET surface area equal to $195\text{ m}^2/\text{g}$ was chosen as the silica filler in the control formulation for the optimized low-rolling resistance compounds. The polysulfide silane coupling agent was added at 6 phr, to compensate for the high surface area of the silica filler. The loading level of zinc oxide and the accelerator to sulfur ratio were also optimized to account for the high surface area silica in these recipes. Based on previous results, this high surface area silica, combined with the adjustments to the previously listed chemicals, provided improved fuel economy as measured by $\tan \delta$ at 60°C , better dry handling as measured by E' at 30°C and increased DIN abrasion resistance²⁴.

In the optimization study, the experimental compound included the same recipe with the exception of the carbon-black filler and processing oil. After reviewing the processing parameters, physical properties and DMA predictors for traction and rolling resistance in the carbon black and silica study, broad aggregate carbon black was selected as the carbon-based filler for the optimization study. In this case, the broad aggregate carbon black filler is used as replacement for the 15 parts per hundred rubber of N234 carbon black in the silica based, low rolling resistance tread compound.

Previous work by these authors demonstrated that the use of sustainable processing oils in tire tread formulations is a promising alternative to petroleum processing oil²⁵. In particular, replacing 10 phr of the aromatic processing oil in a low rolling resistance tread compound with vulcanized vegetable oil was advantageous based upon the resulting performance predictors and physical properties. Compounds using vulcanized vegetable oil showed improvement in rolling resistance predictors based upon DMA analyses. The vulcanized vegetable oil (VVO) used in this optimization study is Neophax A VVO and contains unsaturated oils from soybean oils, which are partially crosslinked (vulcanized) with sulfur. In the optimized formulation, 10phr of the TDAE processing oil is replaced by VVO.

Based on the positive results observed separately by VVO and broad aggregate carbon black, it was desired to determine if synergistic effects could be obtained by combining a unique functionalized polymer, a high surface area precipitated silica and broad aggregate carbon black with the VVO. The optimized recipe formulations are shown in Table 5, where the unique recipe ingredients are highlighted. In the optimized study, the zinc oxide, stearic acid and fatty acid

processing aid were moved to the second mixing pass to prevent reactions with the polymer, carbon black and silica due to the chemical modification of the functionalized polymer.

Table 5: Optimized Recipe Formulation (parts per hundred rubber, by weight)

Formulation		
Component	Optimization Study Control Formulation (phr)	Optimized Formulation (phr)
Functionalized S-SBR	75	75
Polybutadiene Rubber	25	25
N234 Carbon Black	15	
Broad Aggregate Size Carbon Black		15
Highly Dispersible Silica	60	60
Silane coupling agent	6	6
TDAE Processing Oil	33.12	23.12
Vulcanized Vegetable Oil		10
Microcrystalline Wax	2	2
Antidegradant	2	2
Antidegradant	0.5	0.5
Zinc Oxide	1.9	1.9
Stearic Acid	2	2
Process Aid	2	2
Sulfur	1.4	1.4
Sulfenamide Accelerator	1.7	1.7
Guanidine Accelerator	2	2
Total phr	229.62	229.62

Key physical properties were compared for the control compound and the optimized, alternative filler compound. Figure 19 compares hardness in Shore A for the as-molded rubber samples and heat aged samples, after conditioning for three weeks at 70°C. Durometer for the optimized formulation was five points higher than the control sample, most likely due to the use of vulcanized oil in the formulation. As expected, the rubber became harder after heat aging and did not show any unusual behavior for the optimized formulation.

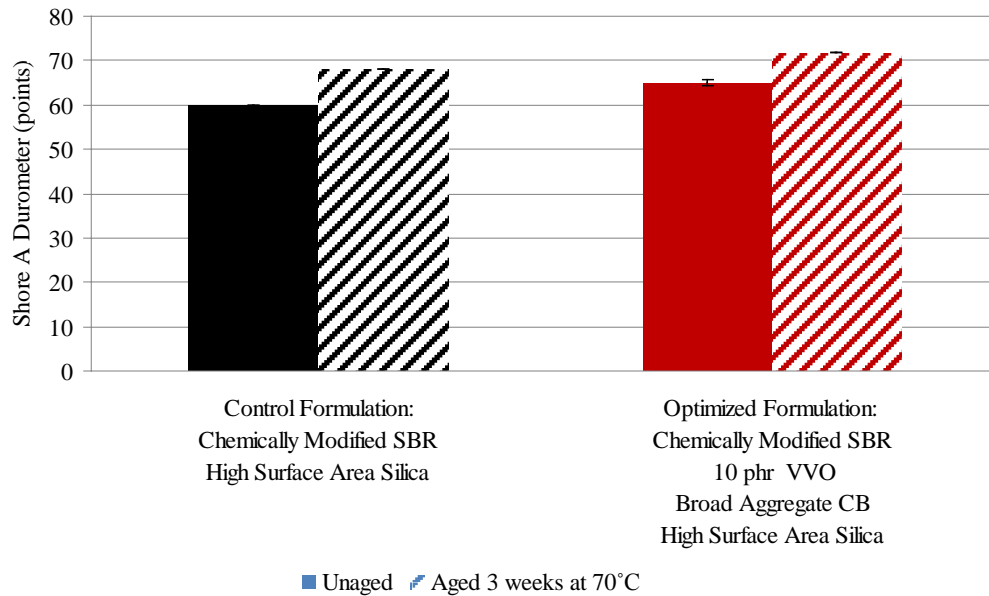


Figure 19: Hardness of control formulation and optimized formulation tread compounds as molded (solid) and after heat aging (striped).

As seen in Figure 20, peel tear resistance using 180-degree geometry at 100°C was identical for both the control and optimized formulation. Figure 21 shows the decrease in percent elongation at break for the optimized formulation using the broad aggregate carbon black in conjunction with the vulcanized vegetable oil. This reduction in elongation is likely caused by the increased vulcanization of the oil and resulting higher durometer compound. Despite the drop by almost 25% in elongation, the optimized formulation is within standard range for physical properties of tread compounds.

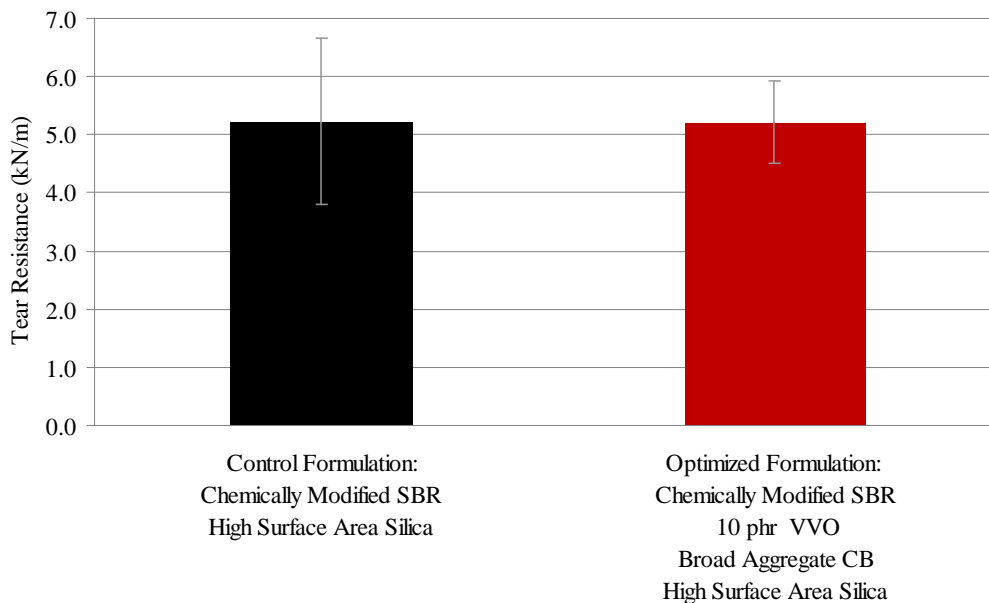


Figure 20: 180° Peel Tear Resistance at 100°C of control formulation and optimized formulation tread compounds as molded.

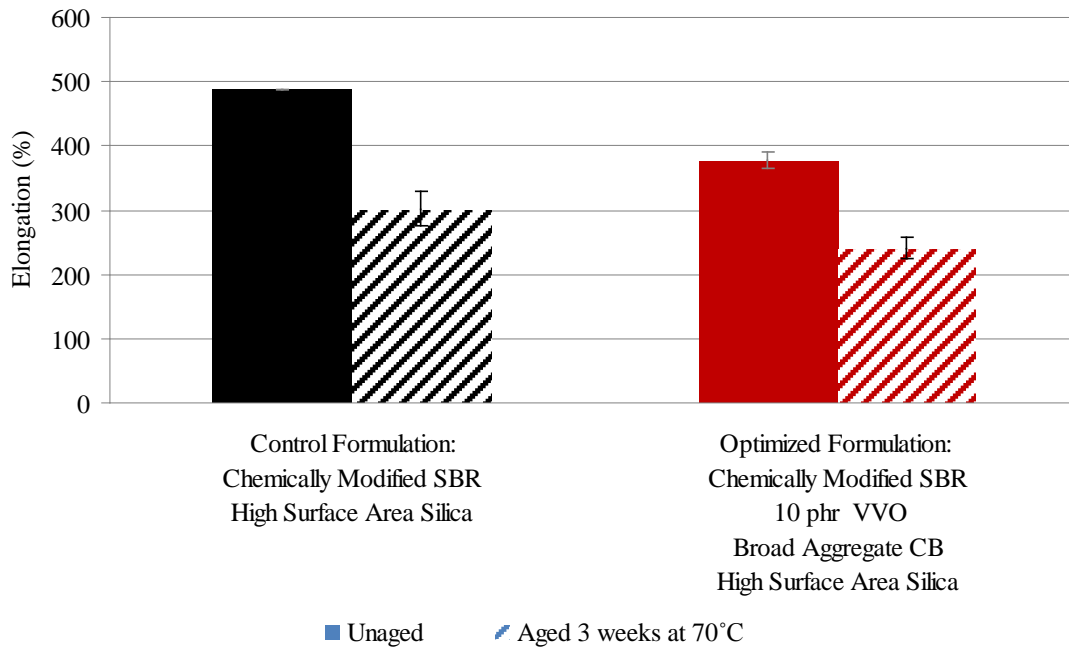


Figure 21: Percent elongation at break of control formulation and optimized formulation tread compounds as molded (solid) and after heat aging (striped).

Since processing parameters and physical properties of the optimized formulation were within acceptable range, viscoelastic properties of the tread compound were analyzed and compared with the control formulation. Figure 22 provides a summary of the performance predictions using DMA in tension. Results were normalized to properties of the control compound with higher numbers indicating preferred improvement in properties (i.e. tan delta at 60°C was adjusted so higher values are better.)

Maintaining performance criteria of dry handling, wet traction, fuel economy and winter traction is critical for tire performance and trade-offs must be managed accordingly. The optimized formulation exhibited very promising results for improving rolling resistance while maintaining or improving the other key areas of performance. By using a chemically modified solution styrene butadiene rubber and high surface area silica in the control recipe, the noted property improvements in Figure 22 signify the exciting result that use of these materials may provide opportunities for further advancements in low rolling resistance tread compounds. Of course, other requirements such as noise, wet handling and wear need to be assessed prior to further developments in this area.

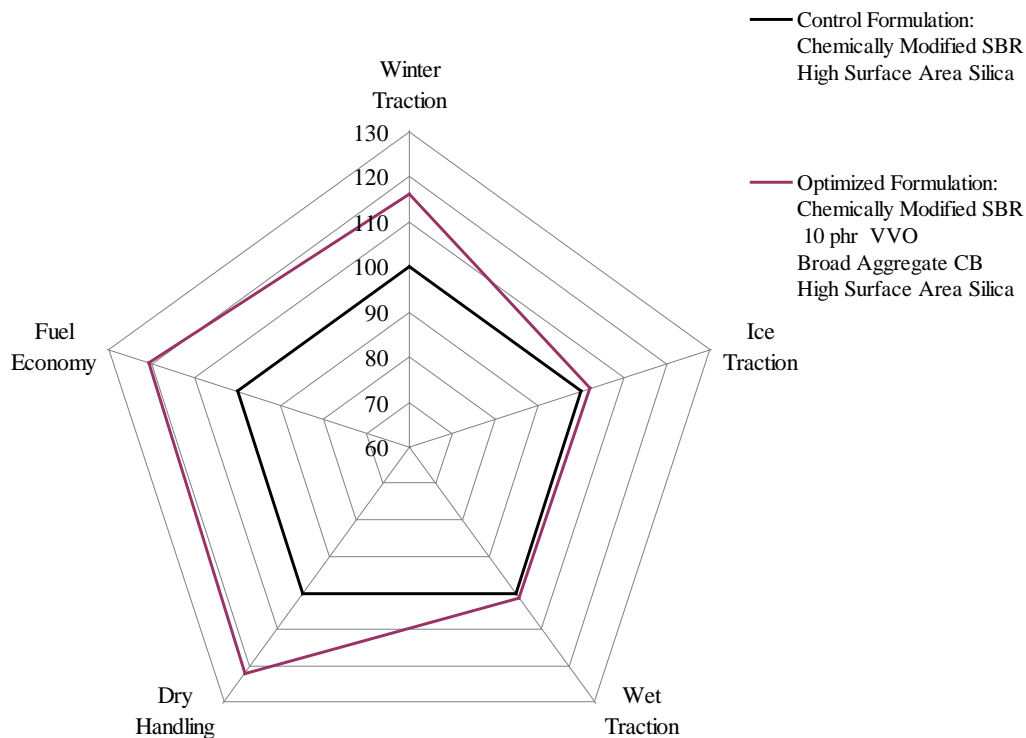


Figure 22: Normalized dynamic mechanical analysis (DMA) performance predictors for key tire attributes.

While all performance criteria including dry traction, ice traction and dry handling are essential to tire performance, there exists a well recognized trade-off between wet traction and rolling resistance which is evident in these novel filler compounds. Figure 23 compares the tread compounds from the three distinct studies discussed in this paper by assessing the performance predictors for wet traction ($\tan \delta$ at 0°C) and rolling resistance ($\tan \delta$ at 60°C). For these two criteria, BR-acrylate terpolymer and hybrid CB-silica fillers showed similar behavior to the silica control formulation. If focusing solely on improving fuel economy, the optimized compound with functionalized S-SBR, VVO, broad aggregate carbon black and high surface area silica has the lowest $\tan \delta$ at 60°C , predicting improved rolling resistance. However, since companies are interested in balancing all attributes and tailoring compounds to specific requirements, other fillers in this study warrant further investigation.

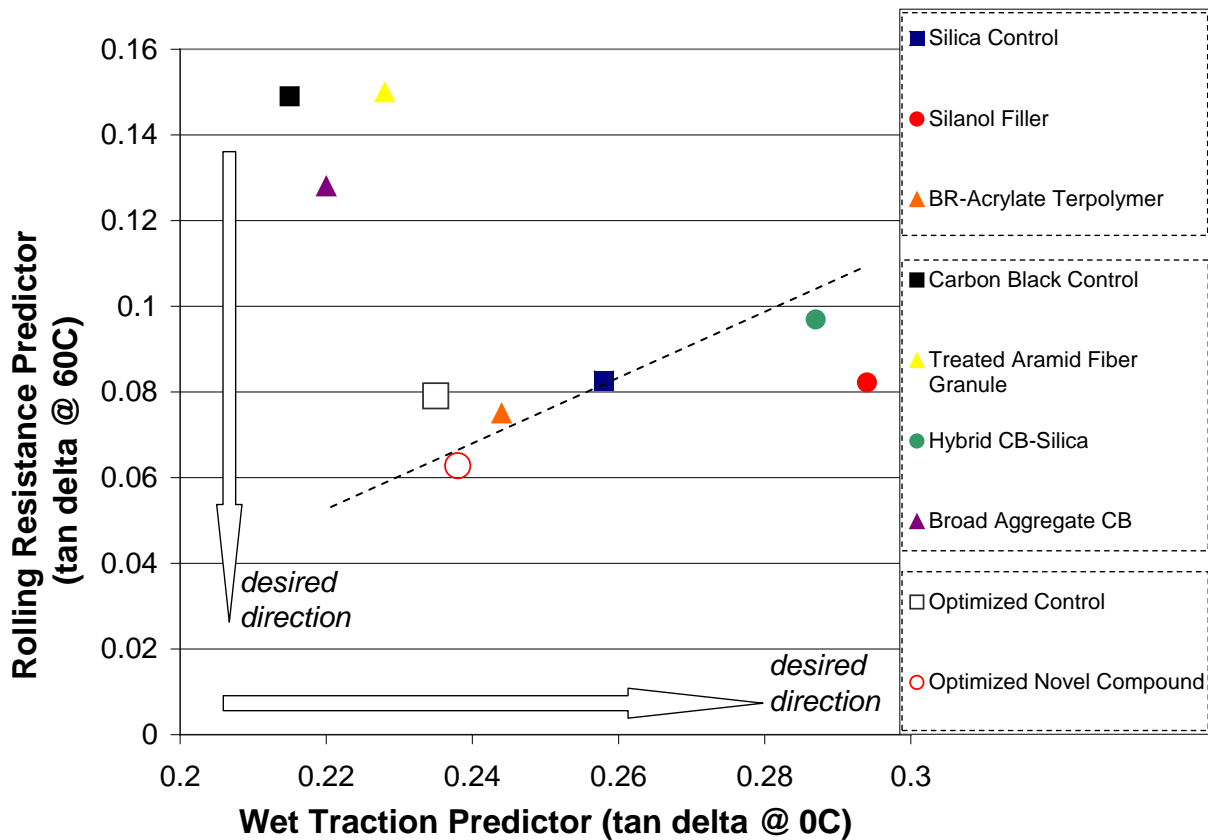


Figure 23: Trade-off comparison of rolling resistance versus wet traction for all formulations.

CONCLUSIONS

Increases in petroleum prices and consumer expectations for fuel economy have had a tremendous impact on the tire-related technical community. With these drivers, original equipment manufacturers, tire companies and chemical suppliers have sought technical solutions to improve the associated energy loss in tires while maintaining other key performance attributes. In an effort to balance the "magic triangle" of all season traction, wear and fuel efficiency, research and development of tread compounds has provided an avenue to explore potential improvements for rolling resistance.

Tread compound formulations typically use on the order of 60-85 parts filler per hundred parts of rubber, in order to provide improvements in wear resistance. Common commercial fillers used in the automotive sector today are carbon black, precipitated silica or a combination therein. Companies and universities have been exploring a range of alternative fillers from chemically treated silicas to nano-scaled minerals that may provide improvements in formulated tread compounds.

This study evaluated two unique fillers in a typical low rolling resistance tread compound using high silica loading levels: silanol filler and BR-acrylate terpolymer. As is expected with new tread compound formulations, use of these alternative fillers provided a trade off in performance properties for anticipated fuel economy, traction and handling. In particular, the BR-acrylate terpolymer exhibited modest improvements for predicted rolling resistance but with noted trade-offs to dry handling performance. Use of silanol filler showed equivalent performance for dynamic mechanical analysis predictors for rolling resistance, with noticeable improvement for wet traction.

To determine if further improvements in fuel efficiency could be identified in carbon black based tread compounds, three additional alternative fillers were analyzed including treated aramid fiber granule, hybrid of carbon black-silica and broad aggregate carbon black. The largest improvements in fuel economy were observed for hybrid carbon black-silica filler, followed by use of broad aggregate carbon black filler. Use of hybrid carbon black-silica showed excellent improvements in winter traction, ice traction and wet traction, but at the expense of dry handling performance. Broad aggregate carbon black was identified as having improvements for predicted rolling resistance, while maintaining other key attributes of traction and handling. Compounds using treated aramid fiber granule added at 2phr exhibited improvement in wet traction without detriment to rolling resistance, as well as a slight enhancement to winter traction relative to the carbon black control.

Lastly, an optimization study was completed based upon the processing, physical properties and performance predictors of the alternative fillers. In this scenario, broad aggregate carbon black was used to replace N200 series carbon black in high silica, low rolling resistance tread compounds. By combining this technology with previously reported success in using vulcanized vegetable oil in tread compounds, a unique tread formulation was compared to the high surface area silica tread compound. The optimized, alternative filler formulations showed very promising results for predicted fuel economy, dry handling and winter traction based on dynamic mechanical analysis. Tan delta at 60°C decreased by 20% for the optimized compound with the broad aggregate carbon black filler and vulcanized vegetable oil, predicting improved rolling resistance. In the areas of wet traction and ice traction, this modified compound exhibited similar performance predictors to the control.

In summary, use of alternative fillers has been shown to provide excellent performance in select areas, based upon interpretation of physical and viscoelastic properties. Incorporation of these alternative fillers needs to be custom developed to maximize the benefits and performance according to the end application. This study demonstrated the potential of using a variety of unique fillers in either carbon black or silica based tread compounds and showed the use of these technologies can improve fuel economy by lowering rolling resistance. By coupling these materials with alternative polymers, oils or other additives, even further improvements may be achieved.

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Appendix A: Tire Tread Formulation (parts per hundred rubber, by weight)

Description	Silica Control	Silanol Filler	BR-Acrylate Terpolymer		Carbon Black Control	Treated Aramid Fiber Granule	Hybrid CB-Silica	Broad Aggregate CB
Loading Type	silica	silica	silica		CB	CB	Dual Phase	CB
1st Pass								
Buna VSL 5025-2 , S-SBR	103.12	103.12	103.12		103.12	103.12	103.12	103.12
Budene 1207, S-BR	25	25	25		25	25	25	25
CRX4210A Dual Phase Filler							75	
Vulcan 1436 Broad Aggregate Size CB								75
Nanoprene B M75OH VP RW			10					
Sulfron 3001						2		
N234 Carbon Black	15	15	15		75	75		
Ultrasil 7000 GR Silica	65	65	65					
Si 69 Silane Coupling Agent	5.2	5.2	5.2				2.7	
Tudalin SX Oil	10	10	10		10	10	10	10
Okerin 7240 Wax	2	2	2		2	2	2	2
6PPD, Antiozonant	2	2	2		2	2	2	2
Wingstay 100, Antiozonant	0.5	0.5	0.5		0.5	0.5	0.5	0.5
Zinc Oxide, Activator	2.5	2.5	2.5		2.5	2.5	2.5	2.5
Stearic Acid, Activator	2	2	2		2	2	2	2
KK49, Process Aid	2	2	2		2	2	2	2
Total PHR Masterbatch #1	234.32	234.32	244.32		224.12	226.12	226.82	224.12
2nd Pass								
Masterbatch #1	234.32	234.32	244.32		224.12	226.12	226.82	224.12
SO1458 trisilanolphenyl POSS		3.5						
Total PHR Masterbatch #2	234.32	237.82	244.32		224.12	226.12	226.82	224.12
Final Pass								
Masterbatch #2	234.32	237.82	244.32		224.12	226.12	226.82	224.12
Sulfur, Curative	2	2	2		2	2	2	2
CBS, Accelerator	1.7	1.7	1.7		1.7	1.7	1.7	1.7
DPG, Accelerator	2	2	2		2	2	2	2
Final PHR	240.02	243.52	250.02		229.82	231.82	232.52	229.82