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Recipient:
PPG Industries
Monroeville Chemical Center
440 College park Drive
Monroeville, PA 15146

Website (if available) www.ppg.com

Award Number: DE-EE0006794

Cost-Sharing Partners: Bridgestone Americas Tire Operations

PI:
Lucas Dos Santos Freire, Ph.D.
Senior Research Engineer
Phone: 724-325-5381
Email: dossantosfreire@ppg.com

Submitted by:
(If other than PI)
Gina Terrago
Program Manager – Government Contracts
Phone: 412-492-5728
Fax: 412-492-5696
Email: terrago@ppg.com

DOE Project Team:

DOE Award Administrator	Brittley Robbins
DOE Project Officer	David Ollett
DOE Project Monitor	David Anderson

Gina Terrago es

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PROJECT OBJECTIVES

PPG Industries, Inc. and Bridgestone Americas Tire Operations (BATO) propose to develop a novel surface-modified silica technology and demonstrate 4-6% improved fuel efficiency of Truck and Bus Radial (TBR) tires built from the technology. The proposed fuel efficiency increase will be achieved while maintaining or improving tear strength and tread wear.

PROJECT SCOPE

The proposed fuel efficiency increase will be achieved while maintaining or improving tear strength and tread wear over the state of the art defined as a carbon black (CB)-filled, primarily Natural Rubber (NR)-based TBR tread compound. This will be achieved by systematically and thoroughly investigating the properties that enable uniform dispersion of silica in both natural and synthetic rubbers. This knowledge will be used to drive the development of new silica surface treatments and rubber formulations to control the phase distribution and/or enhance the dispersion of fillers throughout the TBR tread compound. The project shall be conducted in three budget periods (BP):

Phase I: CONTROLLING DISPERSION.

The objective of BP 1 is to understand how different silica surface chemistries and surface areas are linked to dispersion performance in different rubber phases including both natural and synthetic rubbers. The team will use model rubber compounds, design of experiments, and statistical analysis to down-select the silica chemistries and surface areas that deliver the most consistent dispersions in various rubbers.

Phase II: DEVELOP NEW TREAD COMPOUND.

The objective of BP 2 is to use the design principles identified in BP 1 to reduce the rolling resistance of a TBR compound by at least 60% compared to carbon black with no decrease in hardness and equal or better tear strength and tread wear. Activities will include formulating TBR compounds using the dispersion knowledge gained in BP 1 and analyzing performance.

The team will then down-select no more than two combinations of silica and rubber formulations to make an experimental tire build and conduct on-tire testing to identify any performance gaps.

Phase III: OPTIMIZING FORMULA FOR ON-TIRE PERFORMANCE.

The objective of BP 3 is to optimize the TBR compound performance and select the final rubber compound formulations for the tire builds that will be delivered to the DOE for independent testing.

Activities include formula optimization followed by another round of tire builds and testing. The ultimate objective is to develop a new TBR tread formulation that is shown to improve fuel efficiency by 4-6% while maintaining or improving tear strength and tread wear.

INTRODUCTION

Precipitated silica is an amorphous particle produced commercially by the acid neutralization of a sodium silicate solution. Highly dispersible silicas (HDS) are used as the main reinforcing filler in passenger treads. In conventional HDS/*in situ* silane systems, HDS and coupling agents such as 3,3'-bis(triethoxy-silylpropyl)tetrasulfide (TESPT) are co-reacted during the rubber compounding process to create a strong interaction between the HDS and the rubber polymers to deliver better tire performance. In recent years, to overcome the VOCs and other issues associated with the HDS/*in situ* silane process, Agilon® Performance Silica came into the market. In the Agilon process, silane coupling agents, as well as other compatibilizers, are pre-reacted onto the silica surface so that tire manufacturers do not need to control this reaction during compounding. For passenger tires, which are synthetic rubber based, Agilon products can reduce rubber mixing time by 36%, eliminate VOCs, and further improve the “magic triangle” of treadwear, traction, and rolling resistance.

When tires are predominantly comprised of natural rubber (NR), as in the case of TBR tires, silicas no longer provide the same benefits as in passenger tires. NR provides the chip and tear resistance essential for TBR applications, but NR contains proteins, organic matter, and metal ion contaminants. These contaminants are believed to interfere with the *in situ* coupling reaction required to effectively disperse silica in non-polar rubber yielding poor filler dispersion, tire performance, and processing properties. Recently, a high surface area Agilon® silica that is able to be dispersed in NR has been developed, which provided dramatic improvements in rolling resistance compared to CB.[1-4] This performance is obtained due to the ability of Agilon to overcome the contaminant problem since the silane coupling reaction is already completed before mixing.

Bridgestone Americas Tire Operations (BATO) evaluated existing Agilon® materials in actual TBR formulas. They identified that further improvements need to be made before Agilon would be truly impactful to the tire industry. The state of the art in TBR compounds are carbon black-reinforced NR/butadiene rubber (BR) blends. The Agilon tested preferentially dispersed into synthetic rubbers and this non-uniform dispersion creates performance issues for NR/synthetic rubber blends. It is hypothesized that if the Agilon process could be used to control silica surface energy and morphology to more uniformly disperse the silica across blends of natural and synthetic rubbers, its use in a greater range of rubber blends would be possible. Subsequently, TBR tires would experience a potential 20-30% reduction in rolling resistance yielding a 4-6% increase in fuel efficiency. This will enable TBR tires with an optimum balance of fuel efficiency, traction, and tread wear, as well as tear strength.

To achieve the goals of this project, we will systematically and thoroughly investigate the properties that enable uniform dispersion of silica in both natural and synthetic rubbers. This knowledge will be used to drive the development of new silica surface treatments and rubber formulations to control the phase distribution and/or enhance the dispersion of fillers throughout the TBR tread compound. By the end of the program, we expect to identify:

- a methodology to controllably and uniformly disperse silica fillers into the various phases of the rubber formula,

- a new surface modified silica technology that reduces the rolling resistance of a TBR tread compound by at least 60% in laboratory testing relative to carbon black technology, and

- a new rubber blend for TBR compounds containing surface modified silica, optimized for on-tire rolling resistance, tear strength, and tread wear performance.

TECHNICAL PROJECT TASKS

Task 1: Controlling Dispersion in Individual Rubber Chemistries

Perform synthesis of new surface-treated silicas, compound silicas in pure rubber compounds, and analyze of the compounds to learn how each silica chemistry/rubber compound interact.

Subtask 1.1: Novel Silica Synthesis

React Silica compatibilizers and coupling agents onto silica particles.

Subtask 1.2: Pure Rubber Compounding and Analysis

Compound the silica samples in the following individual polymers: natural rubber (NR), butadiene rubber (BR) and styrene-butadiene rubber (SBR).

Task 2: Controlling Dispersion in Model Rubber Blends

Verify the predictive capability of the individual rubber data and select up to three experimental candidates that most consistently disperse in a range of polymers.

Subtask 2.1: Iterative Silica Synthesis

Subtask 1.2 will be re-iterated with additional silica compatibilizers and coupling agents or changes in surface area.

Subtask 2.2: Compounding Blends of Rubber

Each of the silicas from Subtask 2.1 will be compounded in binary blends of NR, BR, and SBR at varying ratios.

Task 3: Developing an Improved TBR Compound at Bench Scale

Develop TBR tread compounds containing up to three of the silicas and polymer blends from Task 2 to deliver a >40% reduction in rolling resistance as measured by tan δ at 60°C compared to an all carbon black-filled natural rubber-based compound. Hardness, tear strength, and tread wear will be evaluated at bench scale.

Task 4: Experimental Tire Build

Generate on-tire data to identify any gaps in the performance of the experimental formulas.

Subtask 4.1: Produce Novel Silica at Pilot Scale

Produce approximately 500 lbs each of up to three silica compositions to support tire builds and on-tire testing.

Subtask 4.2: Produce Novel Tread Compounds and Tires

The silica samples from Subtask 4.1. will be compounded in up to two TBR tread formulations previously selected. Up to two novel formulations and one control formulation will be used to tread approximately 30 test tires.

Task 5: On-tire Testing

Generate on-tire data to identify any gaps in the performance of the experimental formulas.

Task 6: Optimize TBR Compound at Bench Scale

Close the gaps in rolling resistance, hardness, tear strength, or tread wear through further formulation and silica modifications as needed.

Task 7: Final Experimental Tire Build

Confirm the improvements and supply baseline and experimental tires to the DOE for independent testing.

Subtask 7.1: Produce Novel Silica at Pilot Scale

Produce the volumes needed to support tire builds and on-tire testing.

Subtask 7.2: Produce Novel Tread Compounds and Tires

Up to two novel formulations and one control formulation will be used to tread approximately 30 test tires.

Task 8: On-Tire Testing

The objective of this task is to generate on-tire data to confirm performance against project goals.

TASK REPORT

Task 1: Controlling Dispersion in Individual Rubber Chemistries

Surface Energy Studies

Silica, by its nature, has a very polar surface. On the other side, rubbers have little polarity. During rubber mixing, distributing the polar silica in non-polar rubber is a challenge. It was hypothesized that surface treatments could cover part of the surface by hydrophobic groups, and reduce the surface energy, thus helping to wet the silica with rubber during mixing and improving silica dispersion. The approach taken focused on determining the effect that different silica surface modifiers have on the surface energy of the silica, and understanding the relationship with silica dispersion in rubber compounds. The surface polarity of several pretreated silicas, prepared for this project with different chemistries was measured. The measurement of surface energy was performed using the Washburn technique and the Fowkes surface energy theory. Half-gram packs of each silica in a standard Kruss FL12 powder cell were tested for wettability with water and diiodomethane, and hexane as the material constant determination liquids. When the Fowkes theory is applied to the contact angle data, the surface energy data shown in Table 1 was determined. Samples JM0316-NG18 and JM0316-NG 4, which do not have any surface treatment, show the highest surface energy as expected. The rest of the samples, contain different proprietary treatments with organic molecules. The chemical treatments reduce the silica surface polarity, therefore reducing the silica surface energy and decreasing the interfacial tension with the hydrophobic rubbers. It can be concluded that the amount that the surface energy is reduced depends on the particular chemistry used to hydrophobate the silica surface. This implies that certain treatments, are more effective than others at reducing the surface energy of the silica surface. The treatments in samples JM0359-1NG and JM0359-4NG turned out to be the ones that reduce the surface energy the most.

Silica	Overall Surface Energy (mJ/m^2)	Polar Component (mJ/m^2)	Dispersive Component (mJ/m^2)	Surface Polarity (%)
JMO316-18NG	66.3	31.1	35.2	46.9
JMO316-14NG	65.0	30.1	34.9	46.3
JMO316-11NG	63.5	28.9	34.6	45.5
JMO316-13NG	59.5	26.0	33.5	43.7
JMO316-17NG	58.2	25.3	32.9	43.5
JMO317-8NG	56.7	24.2	32.5	42.6
JMO316-16NG	56.4	24.1	32.3	42.8
JMO317-7NG	53.2	21.7	31.5	40.8
JMO359-3NG	52.5	21.4	31.1	40.7
JMO316-12NG	50.2	19.7	30.6	39.1
JMO359-4NG	48.9	18.7	30.2	38.2
JMO359-1NG	44.3	15.0	29.3	33.9

Table 1. Surface energy of silica prototypes.

The surface energy of unfilled natural rubber, SSBR and butadiene rubber samples was also measured at different temperatures (room temperature and rubber mixing temperatures). The data obtained is shown in Table 2. As it can be seen in the Table, the surface energies of all rubber are much lower than those of the silica samples. The silica samples, even though they are partially hydrophobated, are all higher in surface energy and surface polarity than any of the rubbers, so interfacial tensions are significant in all cases. This is due to the hydrophobic nature of hydrocarbon based rubbers. These results indicates that, to reduce to a minimum the interfacial tension between any of the traditional rubbers used in truck tires, the surface energy of the silica has to be reduced as much as possible. We hypothesized that the interfacial tension has to be reduced as much as possible, to increase the wetting of the silica surface by the rubbers, and improve dispersion.

Rubber	Temperature (°C)	Overall Surface Energy (mJ/m^2)	Polar Component (mJ/m^2)	Dispersive Component (mJ/m^2)	Surface Polarity (%)
Natural Rubber	22	33.3	8.2	25.1	24.6
	150	28.3	6.4	21.9	22.5
	170	27.1	5.9	21.2	21.9
SSBR	22	27.8	5.5	22.3	19.8
	150	23.6	4.1	19.5	17.4
	170	22.7	3.8	19.0	16.5
Polybutadiene	22	25.7	3.9	21.8	15.2
	150	21.8	3.0	18.8	13.8
	170	20.9	2.8	18.2	13.2

Table 2. Surface energy of rubbers commonly used in tires.

Different analytical techniques can be used to measure dispersion improvements in rubber compounds. One of those techniques is to measure the low strain modulus of the compound. A typical strain sweep curve is shown in Figure 1. The reduction in modulus with increasing strain is known as Payne effect and is due to the breakage of the filler network with increasing strain. The higher the filler-filler interaction, the higher the low strain modulus. Improved silica dispersion reduces the filler-filler network, and the low strain modulus is reduced.

Compounding results of the silica samples from Table 1 was performed in NR compounds containing 60phr (parts per hundred rubber) of silica. The relationship observed between silica surface energy and G’ at 1% strain determined by ARES is shown in Figure 2. We can observe in the plot that the filler-filler network is reduced (improved dispersion) with reduced silica surface energy and reduced interfacial tension with the NR.

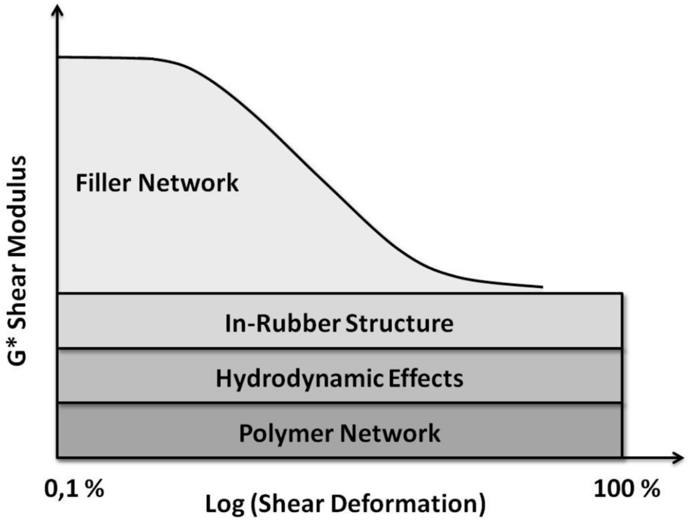


Figure 1. Payne effect: reduction of dynamic stiffness with increasing strain.

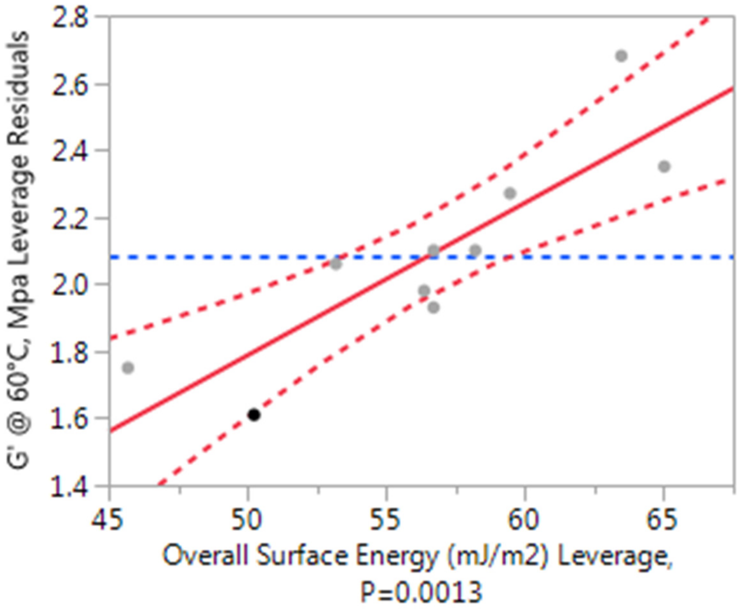


Figure 2. G' at 1% strain (indicator of filler-filler interaction) vs. silica surface energy.

These results demonstrate that silica surface energy depends on the nature of the treatment used, and chemistries which provide the highest reduction in surface energy are preferred to optimize dispersion. We have established the relationship between surface energy of silica particles and the low strain modulus (dispersion indicator) of the NR-based model compound used in this project.

Task 2: Controlling Dispersion in Model Rubber Blends

During Task 1 of the project, we observed that reducing the surface energy of silica reduces the filler-filler interaction and provides better dispersion in single polymer compounds. During Task 2, we investigated the dispersion of selected silica prototypes in binary polymer blends of NR/BR and NR/SBR. To directly evaluate the dispersion of filler in compounds containing polymer blends, we performed microscopy and NMR analysis on filled rubber compounds.

Scanning Electron Microscopy (SEM)

Rubber compounds were prepared containing 50/50 NR/BR and NR/SBR blends. Fillers used included carbon black (N-234), untreated silica (Hi-Sil® 190G), commercially available treated silica (Agilon® 458G), and two prototype treated silica samples. Rubber mixing was performed in a 1.5L lab mixer equipped with 4-wing tangential rotors and the mixing procedure consisted in two non-productive mixes followed by a productive mix (curatives added). The rubber samples prepared contained only 25phr (parts per hundred rubber) of silica, since previous experience indicated that this amount of filler is adequate to provide a good contrast in microscopy observations.

The final cured samples were evaluated by SEM. In the SEM images, the white phase corresponds to the natural rubber phase, and the dark phase correspond to the synthetic rubber (BR or SBR).

Figure 3 shows SEM images of samples filled with carbon black. It can be seen that in the NR/SBR blend, CB shows a preference towards the SBR phase (dark). In the NR/BR blend, CB does not have a significant preference for any phase, or it has a slight preference towards the BR (dark) phase. We can conclude that CB affinity towards the polymers is SBR>NR≈BR.

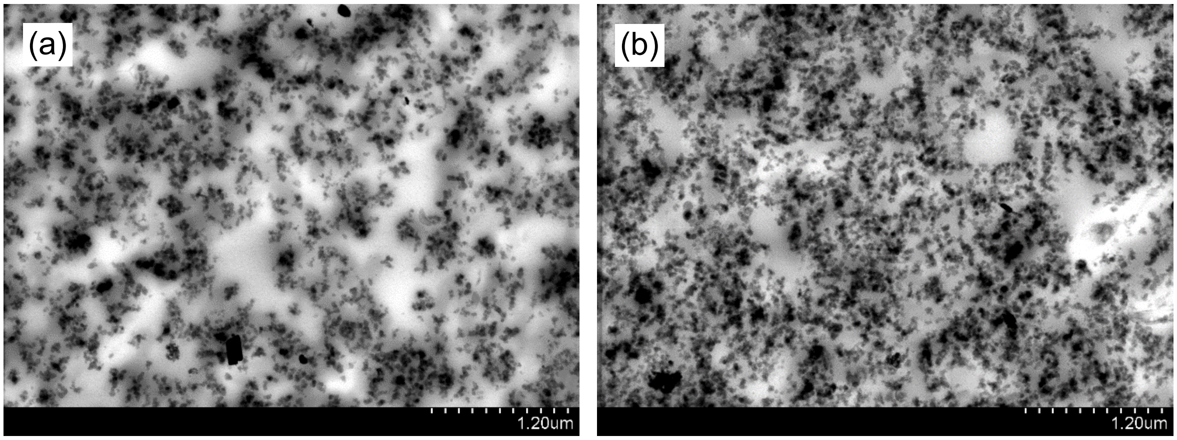


Figure 3. SEM images of carbon black filled compounds. (a) NR/SBR; (b) NR/BR.

Figure 4 shows SEM images of samples filled with untreated silica. When looking at the microscopy images, it can be observed that for the NR/SBR blend, silica has a preference towards the SBR phase, as in the case of CB. However, in the NR/BR blend, silica has a definite preference towards the NR phase. The silica preference towards the rubber phases is clearly SBR>NR>BR.

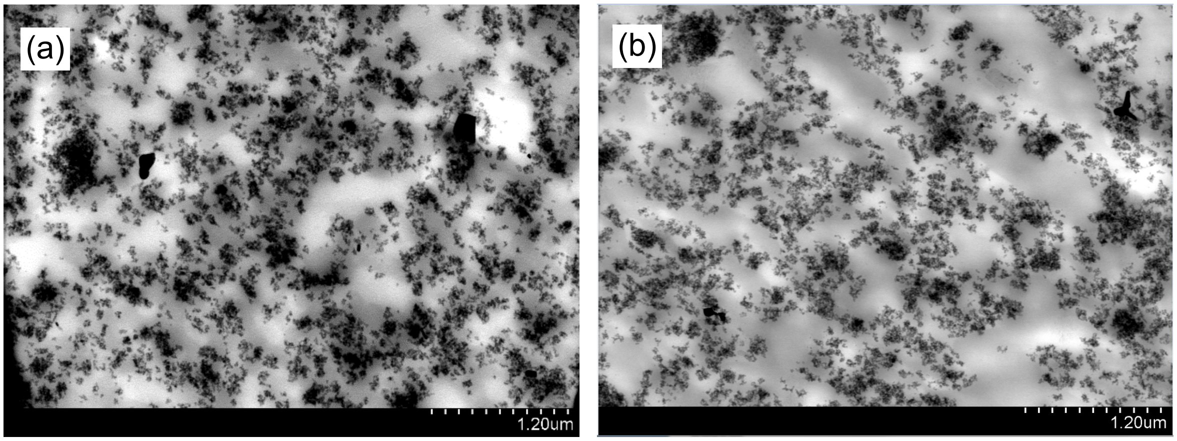


Figure 4. SEM images of untreated silica filled compounds. (a) NR/SBR; (b) NR/BR.

Figure 5 shows SEM images of samples filled with a commercially available treated silica. In this case, the tendency is similar to untreated silica, but with lower definition in the preference towards each phase. In the NR/SBR compound, we can observe a tendency for the silica to preferentially disperse in the SBR phase, but also there is some silica in the NR phase. In the NR/BR compound, while the silica shows a preference towards the NR phase, some of it disperses in the BR phase. These results show that treated silica has a better distribution in the two polymer phases than the untreated silica.

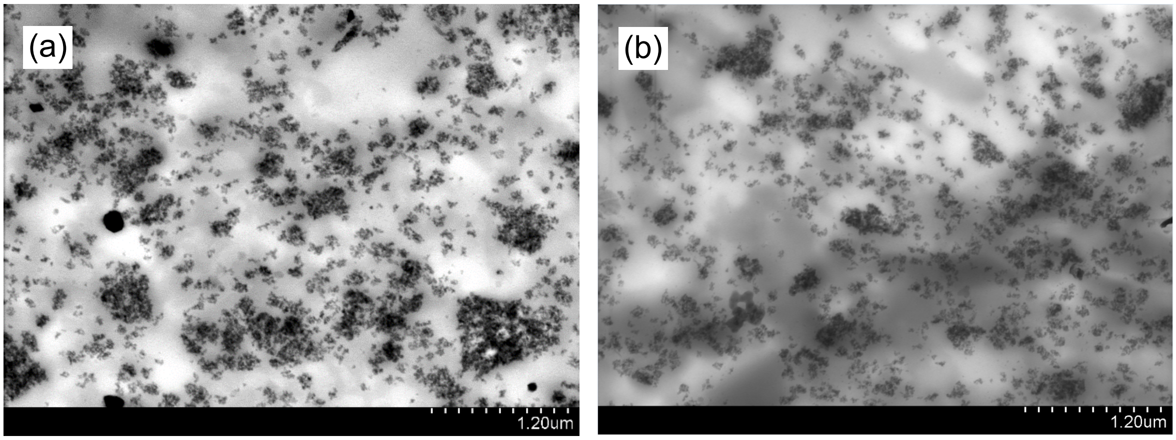


Figure 5. SEM images of commercial treated silica filled compounds. (a) NR/SBR; (b) NR/BR.

Figures 6 and 7 show the SEM images for two silica prototypes selected for this study, which show a similar behavior than the commercially available treated silica. While in the NR/SBR blends both prototypes show a good distribution between the two polymer phases, in the NR/BR blends there is a preference for the fillers towards the NR phase.

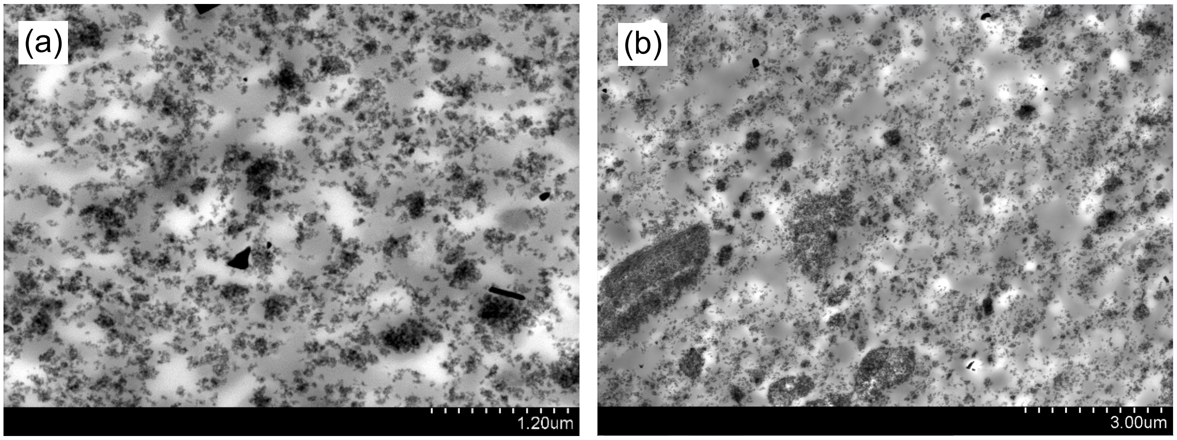


Figure 6. SEM images of treated silica (JM0359-1NG) filled compounds. (a) NR/SBR; (b) NR/BR.

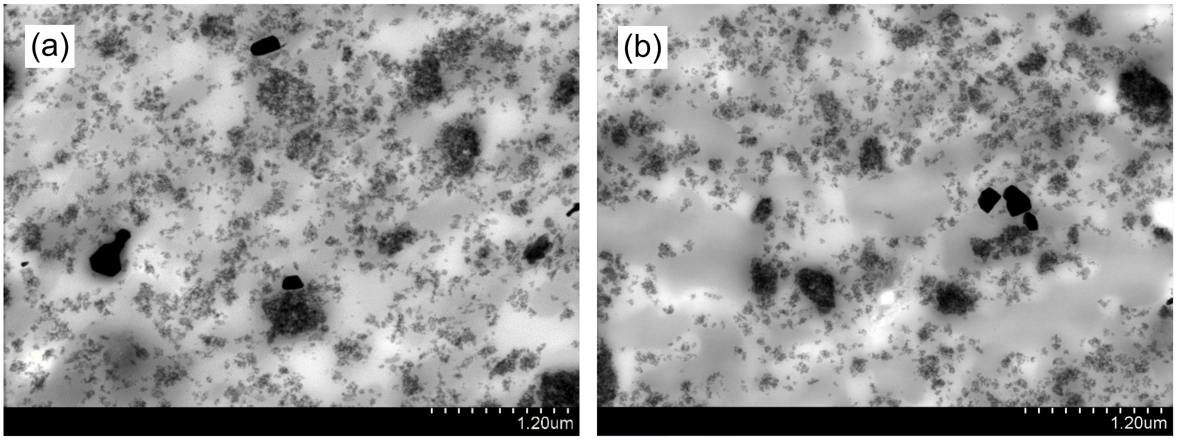


Figure 7. SEM images of treated silica (JM0366-1NG) filled compounds. (a) NR/SBR; (b) NR/BR.

NMR Studies

For this study, rubber compounds were prepared which were comprised also of 50/50 NR/BR and NR/SBR blends. Fillers used included carbon black (N-234), untreated silica (Hi-Sil® 190G), commercially available treated silica (Agilon® 458G), and two prototype treated silica samples. Mixing was performed in a lab mixer and the mixing procedure consisted in two non-productive mixes followed by a productive mix. The main difference with the rubber samples prepared for SEM studies, is that in this case, the rubber samples were prepared using 60phr (parts per hundred rubber) of filler. This was performed in this way because this is a more standard loading, and no contrast for microscopy was required.

Rubber samples were taken after each mixing stage and analyzed by ^{1}H NMR. To perform the composition analysis by ^{1}H NMR, first, the samples were submerged in toluene and the unbound rubber was extracted. Later, ^{1}H NMR analysis was performed on the extracted rubber (unbound rubber) and on the insoluble rubber (bound rubber).

With this technique, the polymer composition of the bound rubber and the unbound rubber was determined to establish which polymer preferentially binds to the filler.

Figure 8 shows the NR content in the bound rubber phase obtained by ^{1}H NMR for the different rubber compounds, after each mixing stage. For example, results show that after the third mixing stage, the bound rubber in the carbon black filled compound has 41% NR and 59% SBR. Since the compounds have overall 50% NR and 50% SBR, an equal distribution of the filler in the two rubber phases would have a 50% NR and 50% SBR content in the bound rubber. The results show that CB has preference towards SBR, in agreement with the microscopy results (see Figure 3.a). Figure 8 shows that initially (after the first stage), untreated silica and the silica prototypes have a tendency to be incorporated in the NR phase (NR content >50%), while CB and Agilon 458G are well distributed in both phases. Upon further mixing, the SBR content in the bound rubber is >50% for carbon black, untreated silica and Agilon 458G, indicating that these fillers have a preference towards the SBR phase. In the case of the silica prototypes, the final composition of the bound rubber is about 50/50 NR/SBR, indicating that the fillers are well distributed in both phases, in agreement with microscopy data.

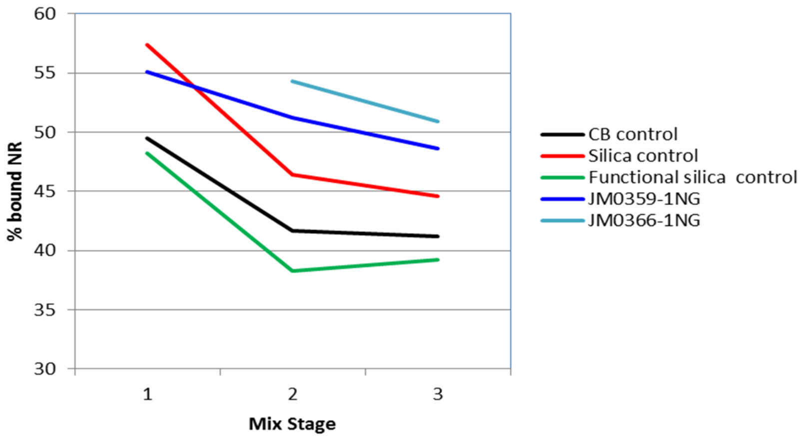


Figure 8. Composition of the bound rubber in NR/SBR compounds obtained by ^{1}H NMR analysis.

In the NR/BR compounds, Figure 9, while CB is similarly distributed in both phases, the silica samples have a tendency to be incorporated in the BR phase. All samples initially (after the first mixing stage) have a preference towards NR, and then slightly shift towards a better dispersion in both phases.

The studies performed to directly observe the distribution of different fillers in binary polymer blends showed that while carbon black preference towards the different polymer phases is SBR>BR≈NR, for commercially available silica samples (treated and untreated) is definitely SBR>NR>BR. The silica prototypes studied dispersed very well in the NR/SBR system, showing a preference in the order SBR=NR>BR.

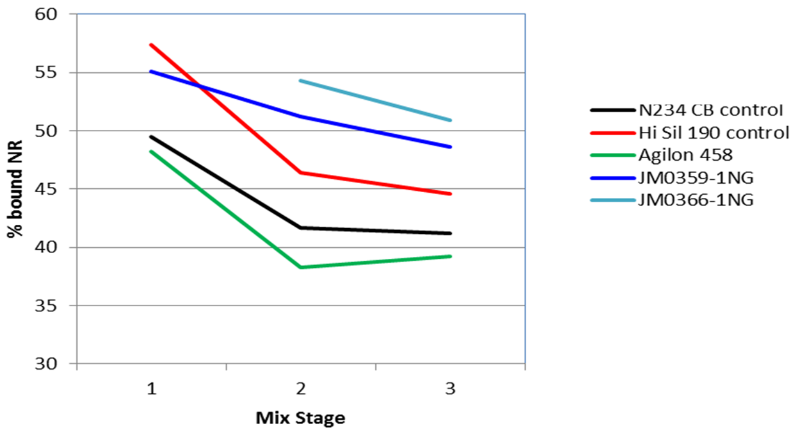


Figure 9. Composition of the bound rubber in NR/BR compounds obtained by ^{1}H NMR analysis.

It can be concluded that the ^{1}H NMR results, for both types of polymers blends (NR/SBR and NR/BR) agree with microscopy data. It must also be considered that while the NMR samples contain 60phr of filler, the samples used in microscopy contain only 25phr of filler. These results are valid for 50/50 NR/BR and NR/SBR polymer blends mixed under the conditions used for this study. A shift on the filler distributions could be obtained under different conditions.

Compound Performance

By using the knowledge learned from studying the surface energy of fillers and studying the behavior of these fillers in polymers blends, we were able to select prototypes which provide significant improvement in lab rolling resistance indicators.

After screening more than fifteen silica prototypes, determining their surface energy and distribution in rubber compounds, four silica prototypes were selected to perform additional in-depth studies. Lab data of single polymer compounds containing these silica prototypes, together with carbon black (N-234), untreated silica (Hi-Sil® 190G) and a commercially available silica (Agilon® 458G) controls is shown in Tables 3 through 5. As it can be seen in Table 3, for the natural rubber (NR) compounds, the four silica prototypes, and the two silica controls, have significant improvement in dispersion measured by Dispergrader compared to carbon black (from 88% to 97-99%). Also, G’ at low strain, which is used as an indicator of filler-filler interaction, is significantly reduced (improved filler dispersion). Other compound performance indicators show that these silica prototypes are promising for further development. Significant improvements in tan δ and rebound (rolling resistance indicators) was obtained, while DIN abrasion and tear strength are not significantly affected.

The same trend can be observed in Tables 4 and 5, where excellent dispersion determined by Dispergrader and G’ at low strain is observed by the silica prototypes in 100% polybutadiene (BR) and 100% styrene-butadiene rubber (SBR) compounds. Dispersion by Dispergrader is equal or better for the silica prototypes than for the CB control and the indication of filler-filler dispersion by G’ at low strain shows that the filler network is largely reduced due to the improved dispersion.

Filler	Carbon Black	Hi-Sil 190G	Agilon 458G	LD0380-1	LD0380-2	LD0381	LD0382
ML(1+4)	85	84	78	84	85	91	61
S'$_{max}$	35.8	35.4	19.3	23.0	32.3	28.8	32.5
S'$_{min}$	4.9	4.9	4.4	4.8	5.5	5.5	3.1
Dispersion, %	87.9	98.5	99.4	99.3	96.9	98.7	99.4
Tensile, MPa	24.5	30.5	19.0	24.1	23.7	26.5	24.1
Elongation, %	375	549	590	603	560	589	426
Modulus @ 100 %, MPa	5.2	3.7	1.5	2.1	3.0	2.4	3.7
Modulus @ 300 %, MPa	22.7	15.4	6.4	8.6	12.4	10.2	16.0
300/100 % Modulus ratio	4.3	4.2	4.4	4.2	4.1	4.3	4.3
Hardness @ 23 °C	79	74	65	71	74	69	68
Hardness @ 100 °C	72	69	54	61	69	60	65
Rebound @ 23 °C	46	54	50	52	53	51	65
Rebound @ 100 °C	58	66	56	66	64	62	79
G' @ 60 °C, MPa	5.2	4.4	1.5	1.7	4.8	2.9	2.1
tan (δ) @ 60 °C	0.200	0.110	0.159	0.127	0.101	0.083	0.048
G' @ 0.5 %, MPa	10.5	6.7	3.2	3.3	7.6	4.9	3.1
Δ G', 0.5 % - 16 %	7.9	4.3	1.8	1.8	4.8	2.7	1.2
tan (δ) @ 1.0 %	0.128	0.076	0.168	0.135	0.067	0.069	0.046
DIN Abrasion Index	100	103	95	114	98	102	105
Strebler Tear (N/mm)	37.7	38.6	45.7	45.7	33.5	16.7	32.0

Table 3. Lab data of silica prototypes in NR based compound.

Filler	Carbon Black	Hi-Sil 190G	Agilon 458G	LD0380-1	LD0380-2	LD0381	LD0382
ML(1+4)	115	141	125	146	139	160	89
S'$_{max}$	44.0	41.0	36.6	43.0	41.5	42.8	37.1
S'$_{min}$	6.9	9.2	7.9	9.4	9.2	11.1	5.1
Dispersion, %	98.2	99.0	98.5	95.0	94.5	96.5	99.7
Tensile, MPa	20.7	19.2	19.9	18.0	21.7	19.4	14.9
Elongation, %	322	496	445	510	550	572	336
Modulus @ 100 %, MPa	4.3	2.8	3.1	3.2	3.6	2.6	3.5
Modulus @ 300 %, MPa	19.0	9.8	11.6	9.3	11.4	8.3	13.0
300/100 % Modulus ratio	4.4	3.5	3.7	2.9	3.2	3.2	3.7
Hardness @ 23 °C	77	75	71	76	75	79	72
Hardness @ 100 °C	75	73	69	73	71	72	71
Rebound @ 23 °C	56	63	68	64	60	61	75
Rebound @ 100 °C	65	67	73	70	62	64	80
G' @ 60 °C, MPa	5.7	5.0	3.6	4.8	5.7	5.3	2.9
tan (δ) @ 60 °C	0.160	0.108	0.075	0.088	0.123	0.110	0.050
G' @ 0.5 %, MPa	9.6	6.7	5.3	7.4	8.3	6.8	3.6
Δ G', 0.5 % - 16 %	6.1	3.8	2.2	3.6	4.9	3.5	1.0
tan (δ) @ 1.0 %	0.138	0.089	0.071	0.077	0.090	0.089	0.048
DIN Abrasion Index	100	118	126	113	116	119	91
Strebler Tear (N/mm)	14.4	23.7	22.0	28.1	36.1	34.8	10.2

Table 4. Lab data of silica prototypes in BR based compound.

Filler	Carbon Black	Hi-Sil 190G	Agilon 458G	LD0380-1	LD0380-2	LD0381	LD0382
ML(1+4)	140	150	120	125	112	134	81
S'$_{max}$	38.9	39.2	37.9	43.3	34.8	40.4	37.4
S'$_{min}$	6.5	8.5	6.0	6.6	5.1	7.1	2.8
Dispersion, %	96.9	96.6	99.2	97.4	92.1	94.1	99.3
Tensile, MPa	24.5	30.5	19.0	24.1	23.7	26.5	24.1
Elongation, %	375	549	590	603	560	589	426
Modulus @ 100 %, MPa	5.2	3.7	1.5	2.1	3.0	2.4	3.7
Modulus @ 300 %, MPa	22.7	15.4	6.4	8.6	12.4	10.2	16.0
300/100 % Modulus ratio	4.3	4.2	4.4	4.2	4.1	4.3	4.3
Hardness @ 23 °C	76	75	74	71	74	74	73
Hardness @ 100 °C	71	72	69	65	69	69	69
Rebound @ 23 °C	43	47	55	55	54	51	56
Rebound @ 100 °C	62	66	69	72	71	60	67
G' @ 60 °C, MPa	4.1	4.0	3.0	2.6	3.5	5.5	3.7
tan (δ) @ 60 °C	0.156	0.122	0.097	0.080	0.081	0.125	0.103
G' @ 0.5 %, MPa	6.9	5.9	4.2	3.6	4.6	8.0	5.2
Δ G', 0.5 % - 16 %	3.9	3.3	2.0	1.2	1.5	4.6	2.4
tan (δ) @ 1.0 %	0.154	0.112	0.085	0.090	0.088	0.094	0.086
DIN Abrasion Index	100	89	102	92	87	90	90
Strebler Tear (N/mm)	13.4	20.7	22.5	20.3	23.1	33.0	32.5

Table 5. Lab data of silica prototypes in SBR based compound.

The compound performance of down-selected silica prototypes in compounds with 50/50 NR/BR and NR/SBR polymer blends is shown in Table 6. Again, a large improvement in dispersion by Dispergrader and reduction in G' at low strain is obtained for the silica prototypes compared to carbon black and untreated silica. Higher rebound, and reduced tan δ indicate that these samples are promising to provide improved tire rolling resistance. Improved DIN abrasion and tear strength was also obtained for these samples.

We have shown in this Task that the selected silica samples present improved dispersion compared to carbon black and untreated silica in most single polymer or polymer blend-based compounds. We have also shown a reason to believe that tire rolling resistance will be improved due to reduced hysteresis observed in the compounds containing treated silica prototypes as fillers.

Task 3: Developing an Improved TBR Compound at Bench Scale

The objective of this task is to use the design principles identified in Tasks 1 and 2 to identify one TBR tread compound formula with a >40% decrease in rolling resistance lab indicators, and +/- 10% hardness, tear strength, and tread wear compared to a carbon black-filled natural rubber-based control. Then, two combinations of silica and rubber formulations would be down-selected to make an experimental tire build and conduct on-tire testing on Tasks 4 and 5.

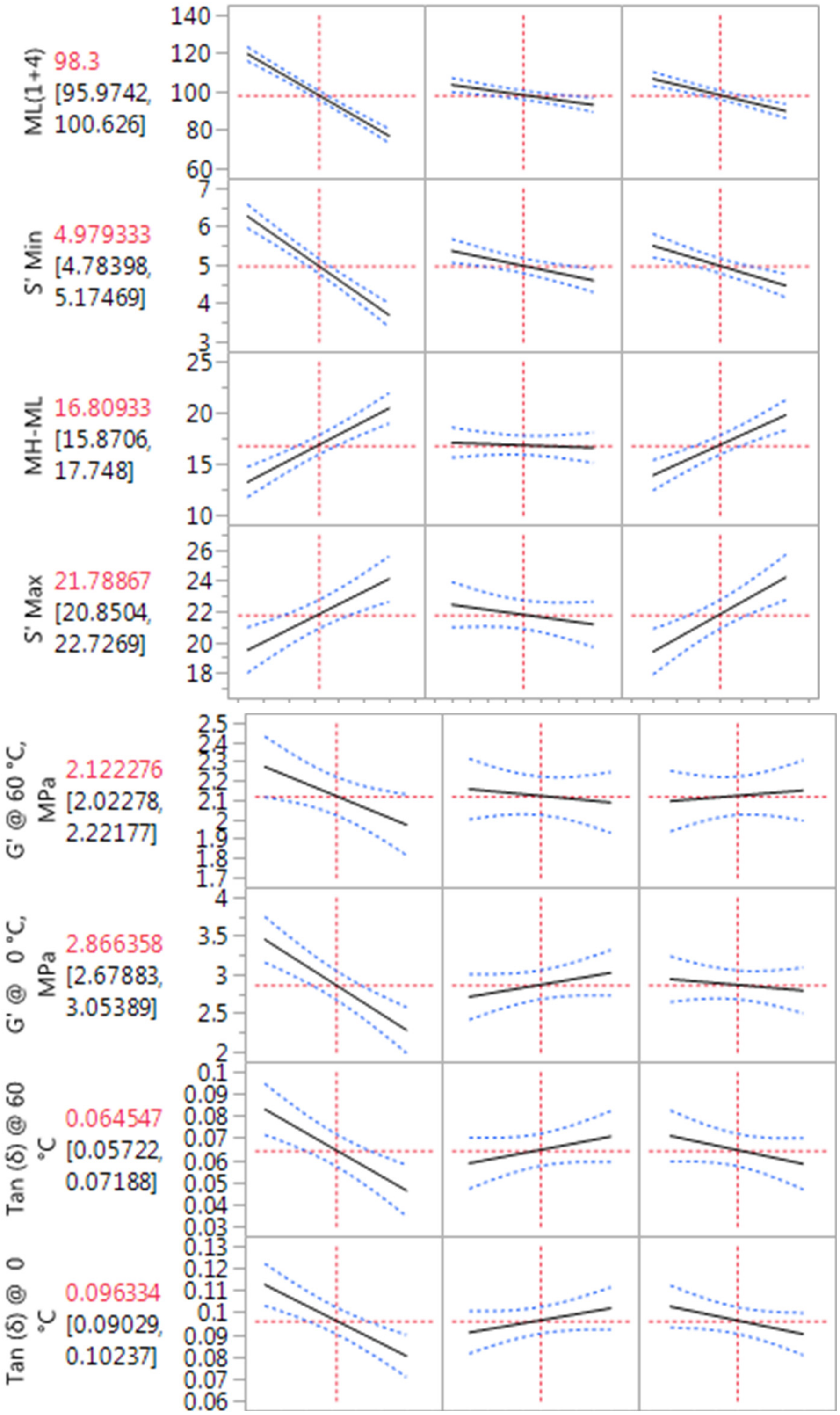
Polymer system	50/50 NR/BR					50/50 NR/SBR				
Filler	Carbon Black	Hi-Sil 190G	Agilon 458G	LD0380 -2	LD0381	Carbon Black	Hi-Sil 190G	Agilon 458G	LD0380 -2	LD0381
ML(1+4)	84	88	71	98	109	91	83	72	73	97
S'_{max}	41.7	31.4	17.5	33.2	27.4	33.2	20.6	16.6	27.4	18.0
S'_{min}	5.3	5.3	4.5	7.6	8.0	5.3	4.3	4.7	4.4	5.9
Dispersion, %	89.3	82.5	93.4	97.1	93.7	70.9	77.4	87.2	77.6	89.3
Tensile, MPa	22.0	21.3	16.1	23.6	14.1	25.5	26.5	20.9	24.8	16.6
Elongation, %	298	525	594	631	683	309	588	515	565	651
Modulus @ 100%, MPa	4.8	3.0	1.6	2.6	1.9	5.1	2.7	2.3	3.2	2.5
Modulus @ 300%, MPa	12.6	10.9	5.9	8.5	6.3	25.4	10.3	9.5	10.6	7.6
300/100% Mod. ratio	2.7	3.6	3.6	3.3	3.3	5.1	3.8	4.2	3.3	3.0
Hardness @ 23 °C	76	70	61	69	67	74	71	65	70	69
Hardness @ 100 °C	72	68	56	66	62	71	67	58	65	62
Rebound @ 23 °C	55	58	53	57	55	44	51	53	53	53
Rebound @ 100 °C	66	64	53	62	58	62	63	64	64	60
G’ @ 60 °C, MPa	5.0	4.3	1.6	4.8	3.1	4.0	3.3	1.8	3.2	2.5
tan (δ) @ 60 °C	0.146	0.098	0.134	0.106	0.122	0.142	0.121	0.117	0.093	0.135
G’ @ 0.5 %, MPa	8.8	5.8	2.5	6.3	4.7	6.9	4.7	2.7	4.3	3.8
Δ G', 0.5 % - 16 %	5.5	3.1	0.9	3.4	2.2	3.9	2.2	0.8	1.8	1.4
tan (δ) @ 1.0 %	0.131	0.081	0.159	0.089	0.120	0.134	0.109	0.132	0.083	0.130
DIN Abrasion Index	100	127	131	128	130	74	71	92	73	70
Strebler Tear (N/mm)	17.3	34.3	43.5	42.6	43.7	20.5	33.8	25.0	38.3	40.1

Table 6. Lab data of silica prototypes in compounds with blends of rubbers.

It is necessary to clarify that the targets for the rolling resistance lab indicators and on-tire RR represent our best estimation of the targets necessary to achieve the project goals for improved fuel efficiency of the project. However, the relationship between lab compound data, tire RR and fuel efficiency is complex, and these estimations may or may not translate directly into the desired outcome.

Task 3 began by determining the optimum values for several silica parameters, using the silica chemistries selected in Task 2, with the objective to produce silica prototypes with the proper balance of performance according to the goals of the project. This is, to produce a compound that delivers a >40% reduction in rolling resistance as measured by tan δ at 60°C compared to an all carbon black-filled natural rubber-based compound, while maintaining hardness, tear strength and tread wear within 10%.

The first activities on Task 3 involved performing design of experiment studies around silica synthesis parameters to determine the optimum silica characteristics. We performed two design of experiments looking at three different silica parameters. Fifteen silica samples for each chemistry were prepared and compound testing was performed at the PPG Silicas rubber lab. The silica prototypes were mixed in a model formulation provided by Bridgestone Americas Tire Operations (BATO). Details from one of the design of experiments are summarized in Figure 10. The Figure shows a few of the trends obtained. As it can be seen in the Figure, correlations between several compound performance parameters with the three silica parameters were established. The second chemistry selected to move to this phase of the project was also investigated in the same way (results not shown).



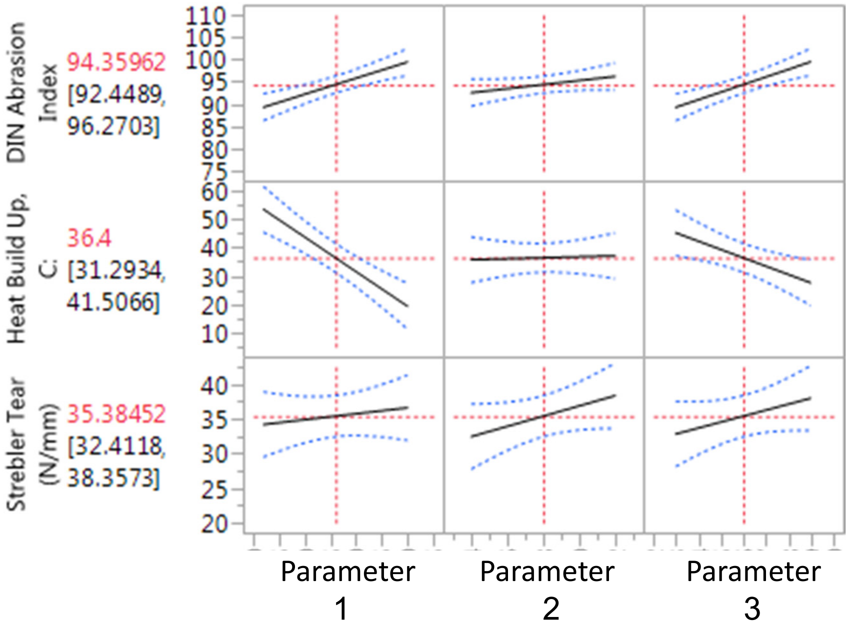


Figure 10. Effect of silica parameters on compound performance.

Based on these responses, the optimum silica parameters, which would provide the best balance of compound performance according to the project targets, were selected. The silica prototypes were scaled-up, and compound work was performed to optimize the tread compounds to be used in the tire build. A large number of rubber mixing studies designed to establish the optimum compound were performed by PPG and by BATO at their respective labs. These studies included:

- Initial cure optimization studies
- Evaluation of mixing conditions (mixing time, mixing temp., etc.)
- Tear improvement study
- Silica loading studies
- Evaluation of slightly modified silica prototypes
- Evaluation of process aids, polymer blends, etc.
- Studies on addition sequence of different compound additives
- Final cure optimization. Necessary because the final compounds had been largely optimized and changed since the original cure studies

Highlights of the results of the optimization work that led to the final compound recipe are summarized here. It can be highlighted that, upon starting with a NR/BR 80/20 polymer blend, we discovered that tear resistance is largely affected by the polymer system, and since the control compound is 100% NR, the prototype compounds need to have 100% NR to achieve the tear target. Twenty percent BR has been added previously with the expectation that it would help to achieve good dispersion and abrasion resistance, but we found that we did not lose much of these properties by switching to 100% NR. The silica loading was increased by 7phr, from the loading used at the start of the project. This was performed to obtain higher stiffness and to have a true one to one replacement by weight of the carbon black replaced from the control. Because the treated silica contains approx. 80% silica, with the remaining 20% being the chemical treatments and moisture, additional 7phr of treated silica are needed to have the same base filler content than the carbon black in the control compound. Finally, curatives were adjusted so that an acceptable scorch safety and a final modulus with little reversion were obtained. The effect of crosslink density (higher with higher curatives loading) was investigated. We observed that, as expected, compound modulus increased with crosslink density. We also observed that at a modulus comparable to the carbon black control, tear and abrasion resistance were comparable to the carbon black control, while we achieved the rolling resistance indicator target (<40% of the control). The curatives loading that provided this optimum balance was selected for the final tread compound formulation. We also observed that it was essential to mix treated silica – NR at low temperature. This is, it should be mixed like NR-carbon black compounds are traditionally mixed, and not like untreated silica / *in situ* silane compounds are traditionally mixed.

After selecting the silica samples (BXR-990 and BXR-991) to scale-up, their performance in the final compound formulation was predicted using the equations obtained from the design of experiments. The expected performance is shown in Table 7. In this study, a carbon black control was not used. Instead, an Agilon 458 commercial treated silica was used. This was done to corroborate that the performance is better than already available commercial treated silicas. It is expected from looking at Table 7, that improved performance will be obtained from the prototypes vs. the currently available commercial product. The developed prototype BXR-990 is expected to provide improved stiffness, rolling resistance, abrasion and tear resistance. Prototype BXR-991 is expected to improve processing, stiffness and tear resistance. Rolling resistance might be worse due to the higher tan δ at 60°C observed, but the higher G' might compensate for this and allow an improved rolling resistance.

Task 4: Experimental Tire Build

The main goal of this Task was to generate on-tire data, and to identify any differences between the on-tire performance and predicted performance from lab indicators. Once the differences are identified, new lab targets for development would be set, and further compound optimization performed prior to the final tire build.

Subtask 4.1: Produce Novel Silica at Pilot Scale

The two silica prototypes (BXR-990 and BXR-991) to be used in the tire build were produced at the PPG Silicas Pilot Plant, in Monroeville, PA. Seven silica precipitations needed to be performed for each silica prototype to produce the 950lbs of each silica prototype required by BATO for the tire build. Both silica samples were characterized and their compound lab performance evaluated at PPG. After confirming that all compound performance indicators were within the predetermined targets, the samples were released for the tire build. The samples were shipped to a re-packer, where they were packed in 25lb low melting bags as required by BATO's tire plant.

Silica	Agilon 458	BXR-990	BXR-991
ML(1+4)	100	108	92
S'_{max}	100	114	104
S'_{min}	100	97	88
S'_{max} - S'_{min}	100	117	107
T50	100	128	106
Tensile	100	117	115
Elongation	100	-	101
Modulus @100 %	100	96	117
Modulus @300 %	100	96	109
300/100 % Mod. ratio	100	100	93
Hardness @23°C	100	103	108
Hardness @100°C	100	102	105
Rebound @23°C	100	100	97
Rebound @100°C	100	100	94
G’ @ 2.0 %, 60C	100	114	144
G’ @ 1.0 %, 30C	100	116	145
tan δ at 60°C	100	88	132
tan δ at 0°C	100	84	98
DIN Abrasion Index	100	105	97
Heat Build Up	100	100	120
Tear strength	100	150	139

Table 7. Normalized lab performance from silica samples for tire build.

Subtask 4.2: Produce Novel Tread Compounds and Tires

The tire build was performed at BATO’s Warren County tire plant in November, 2016. The control compound formulation has 100% natural rubber and 46phr of carbon black. In the silica formulations, 37phr of silica and 15phr of carbon black were used as filler. Also, the cure package loading was slightly increased to accommodate for absorption of curatives in the silica surface, and to obtain compounds with comparable stiffness. Rubber mixing at the plant proceeded as expected. The silica based compounds processing was comparable to the processing of the carbon black control. All three formulations were mixed using similar mixing times and temperatures, and they showed very comparable energy consumption. The silica compounds had slightly higher viscosity, but the higher viscosity was not significant and processing was still acceptable.

Lab compound data of the tread compounds is shown in Table 8. The Table shows data for the CB control, the two silica prototypes, and normalized data for both silica prototypes. The data shows, once again, that the viscosity of the silica prototype is slightly higher than the CB control. Tensile strength is similar for all samples. The silica samples have slightly higher stiffness than the CB control, but within the 10% target. Tear strength of the silica compounds is similar to the CB control (within 10%), except for one of the prototypes at high temperature. Hysteresis (tan δ at 60°C), is 47% and 40% lower than the CB control. The wear indicator shows a slight deficiency (10% and 7%) for the silica prototypes, but still within the target (no more than 10% deficiency). The results are comparable (within error) to those obtained previously at the PPG Silicas rubber lab, and within the lab performance targets set for the project.

The results shown in Table 8 show that we successfully achieved to project goal to develop TBR silica-filled tread compounds with a >40% reduction in rolling resistance as measured by tan δ at 60°C compared to an all carbon black-filled natural rubber-based compound, while maintaining hardness, tear strength, and tread wear within 10% from the control.

	Parameter	CB control	BXR-990	BXR-991
Viscosity		100	112	113
Rheometer	MH-ML	100	124	127
	T50	100	82	82
	T90	100	96	91
Hardness	Index	100	108	109
Tensile test at 25°C	Mod300	100	102	90
	Elongation	100	101	105
	Tensile	100	102	103
	Tensile x elongation	100	102	108
Tensile test at 100°C	Mod300	100	109	93
	Elongation	100	86	104
	Tensile	100	89	100
	Tensile x elongation	100	77	104
Tear, 25°C	Load	100	95	108
Tear, 100°C	Load	100	81	96
Temp. Sweep	E' @ 30	100	104	119
Temp. Sweep	Tan δ @ 60°C	100	53	60
Lab wear	index	100	90	93

Table 8. Normalized lab compound data of tire treads.

Task 5: On-tire Testing

Tires with the prototype tread compounds were built using an Ecopia R197 295/75R22.5 carcass. The two novel silica prototypes and the all-natural rubber/carbon black control formulation were used to tread 36 test tires (12 for each tread compound). The tires were used for rolling resistance test, indoor wear test, section and footprint analysis, and several endurance and high speed tests to evaluate the integrity of the treads. Actual tire data is shown in Table 9.

The Table shows that the prototype silicas achieved 14% and 16% reduction in rolling resistance. Also, the silica compounds showed better performance than the carbon black control in the endurance and high speed tests. It is hypothesized that this is because the silica compounds, with lower hysteresis, generate less heat and run at colder temperatures.

Test	CB Control	BXR-990	BXR-991	990 Index	991 Index
RRC					
Average 3 tires	4.62	3.90	3.99	84	86
St Dev	0.0525	0.0309	0.0368	-	-
QC Endurance					
Final Step	10	10	10	=	=
Total Mileage	4219	4752	4600	+	+
Total Hours	102.9	112.2	115.9	+	+
Removal Code	Tread Area	Tread Area	Tread Area		
New Endurance					
Final Step	10	10	10	=	=
Total Mileage	4450	4450	4450	=	=
Total Hours	89	89	89	=	=
Removal Code	Test Complete	Test Complete	Test Complete	=	=
High Speed					
Mileage	287	287	287	=	=
Removal Speed	101.2	101	101.1	=	=
Removal Code	Tread Area	Test Complete	Test Complete	+	+

Table 9. Tire data.

Tire performance relative to Task 5 targets is shown in Table 10. It can be seen that the hardness and tear targets were achieved. While rolling resistance is slightly higher than the target (16% reduction vs. 20% reduction target), the improvement versus the control are significant. Furthermore, there is evidence that there is a good probability of achieving 20% reduction by the end of the project. First, we had already observed in the lab that by simply reducing the filler loading from 37phr to 35phr, hardness, tear and abrasion resistance are closer to the control, and the rolling resistance indicator, tan δ at 60°C, is reduced another 19%. Extrapolating the 47% improvement in tan δ at 60°C, and 16% improvement in rolling resistance obtained in the tires, this is the additional reduction in hysteresis needed to achieve 20% reduction in rolling resistance. Additionally, even if a 20% reduction in rolling resistance were not achieved, according to the literature, it is probable that we might already achieve about 5% fuel efficiency improvement with the 16% improvement in rolling resistance already obtained.[5,6]

Test	Target	BXR-990	BXR-991
Hardness	± 10 %	108	109
Tear strength	± 10 %	95	108
RR	≤ 80 %	84	86
Tire Wear	± 10 %	67	75

Table 10. Actual tire data against targets.

Regarding tire wear, traditional lab indicators provide trends for wear performance but may, in certain cases, lack the necessary sensitivity to compare across differing compound designs; in this case, different filler systems. Based on this, we can conclude that we should optimize all parameters that may relate to tire wear (tear, tensile strength, modulus, etc.) in addition to lab wear indicators for Task 6. From Task 3, multiple compound properties have been identified for potential optimization and thus improvement of tire performance.

It is also relevant to note here that the goal of Task 5 was to generate tire data and evaluate the correlation of this data to lab-based tire performance indicators. Thus the correlations found here will be used during Task 6, as previously mentioned, to optimize all lab-based tire performance indicators in order to simultaneously achieve all tire performance targets for the project.

Task 6: Optimize TBR Compound at Bench Scale

Based on the tire build results from Task 5, a study to reduce the silica loading was performed. The goal was to better match the hardness and viscosity to the carbon black control, improve rolling resistance, and improve abrasion and tear strength through the reduction in hardness. Results are shown in Table 11. The majority of the studies during Task 6 were performed with BXR-990, and the learnings would be extrapolated to BXR-991, if we were to decide eventually to proceed to the final tire build with BXR-991. It should be mentioned that these experiments were started before obtaining the final results from the tire build in Task 5.

		Tire build value	Optimized value
viscosity		100	94
Rheometer	MH-ML T50 T90	100 100 100	93 96 102
Hardness	Index	100	94
Tensile test at 25°C	Mod300 Elongation Tensile Tensile x elongation	100 100 100 100	122 94 103 99
Tear, 25°C	Load	100	102
Tear, 100°C	Load	100	93
Temp. Sweep	E' @ 60	100	95
Temp. Sweep	Tan δ @ 60°C	100	82
Lab wear	index	100	107

Table 11. Normalized lab data of compound with improved loading of BXR-990 silica.

Subsequently, a DOE study was performed to further optimize a previously identified silica parameter (Parameter 1), silica loading and sulfur loading in the compound. Parameter 1, silica loading and crosslink density are different ways to tweak the compound stiffness, while providing different balance of performance properties. The variation of the most important compound properties as a function of the DOE factors is shown in Figure 11. It can be seen in the plots, that by reducing the Parameter 1, and reducing the filler loading, we can maintain the dynamic modulus, and hysteresis, while significantly improving tear strength. If enough hardness is achieved by reducing the Parameter 1, then crosslink density can be reduced by reducing the sulfur content in the compound to further improve tear strength. Due to the variability in lab DIN abrasion data, not much can be reliably predicted on how tire wear would change.

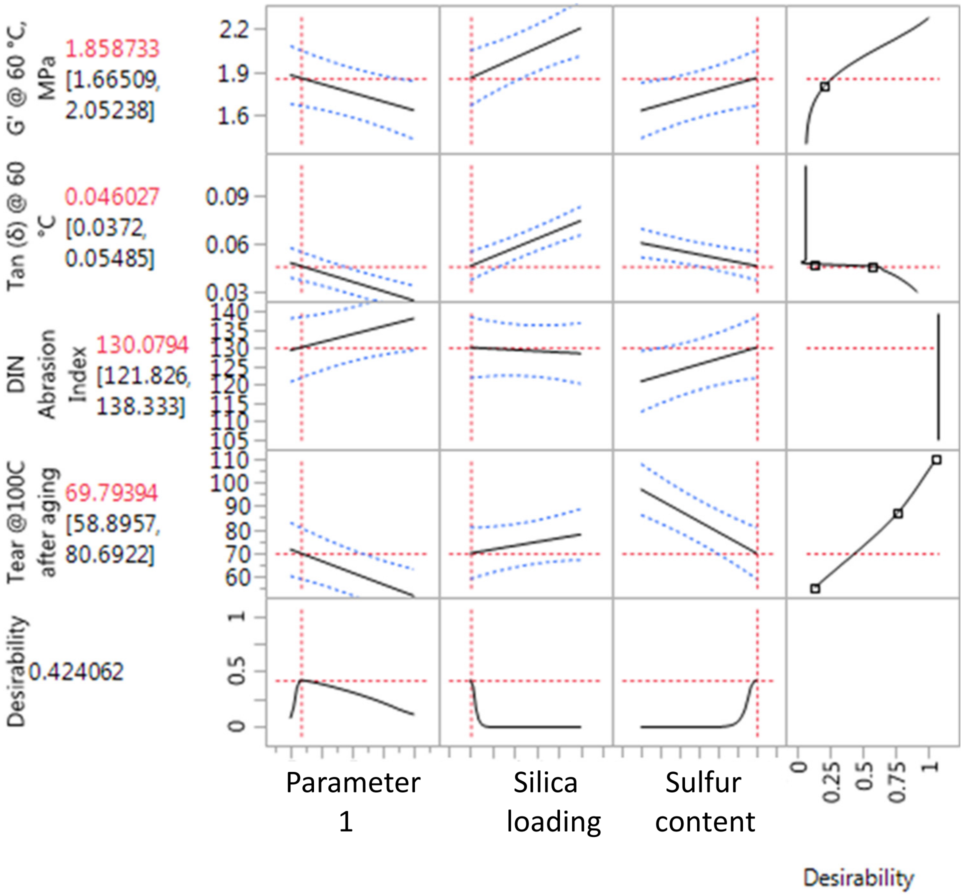


Figure 11. DOE study. Response of main lab compound performance indicators.

Later, PPG performed seven additional compound studies to further determine the optimum filler and sulfur loadings, determine the level of other curatives, and the mixing procedure. The optimized compound formulation and mixing conditions were shared and discussed with Bridgestone Tire America Operations (BATO), and BATO verified the results obtained by PPG.

Selected results obtained by BATO using the new prototype (BXR-1006) with the formulation to be used in the tire build, is shown in Table 12. The three compound recipes shown in the Table are slightly different. The first column shows the carbon black control that was used in the tire build during Task 4 and that will be used in the tire build in Task 7. The second column shows the silica compound that was used in the tire build in Task 4, containing the BXR-990 silica prototype. Finally, the last column shows the new prototype with the new, optimized formulation for this prototype. It can be seen that the new compound based on BXR-1006 significantly improves tear resistance and abrasion compared to the silica compound from the Task 4 tire build. The abrasion resistance and hot tear strength are now equivalent to the carbon black control. This improvement was obtained while maintaining the improved tan δ and other properties. It was also determined that both PPG and BATO could observe similar performance improvements independently in both labs.

Filler		CB	BXR-990	BXR-1006
Cure	ML	100	106	118
	MH	100	120	123
	MH-ML	100	123	124
	T50	100	141	134
RPA	Viscosity	100	110	120
Hardness	Shore A	100	104	99
wear	index	100	76	100
Tensile properties @ 25°C	Mod100	100	135	113
	Mod300	100	108	90
	Strain @ break	100	99	111
	Tensile strength	100	108	115
Tensile properties, Aged @ 100°C	Mod100	100	120	101
	Mod300	100	104	84
	Strain @ break	100	85	101
	Tensile strength	100	86	94
Tear - Die B @ 25°C	Load	100	106	111
Tear - Aged @ 100°C	Load	100	80	103
Strain Sweep @ 60°C	E'	100	106	114
	Tan δ	100	64	65

Table 12. Normalized lab data of compound with optimized silica prototype and adjusted filler loading.

In summary, during Task 5 we concluded that the tires containing silica-filled tread compounds achieved all the projects targets, except tire wear. Through a systematic optimization of the silica prototype, compound filler loading and cure adjustment, we were able to develop a new silica prototype and tread compound which showed significant improvements in mechanical properties in the lab, while maintaining other properties. Compound testing of the new silica prototype (BXR-1006) was completed and it was concluded that it could provide significant improvements in tear strength and lab abrasion compared to the prototypes prepared during Task 4. This is critical because these were the deficiencies observed earlier, and these new results indicate that we might be able to achieve the final on-tire performance goals for the project.

Task 7: Final Experimental Tire Build

Subtask 7.1: Produce Novel Silica at Pilot Scale

The manufacturing of the silica needed for the final tire build was performed and completed at the PPG Silicas Pilot Plant in Monroeville, PA. A total of 3,060 lbs of BXR-1006 was manufactured. To produce this large amount of material, several silica precipitation batches were necessary. Figure 12 shows some of the most important characterization parameters for all the campaign batches made. It can be seen that, except for the fifth batch, which was discarded, good reproducibility was obtained at the pilot plant. The range for the samples are shown in Table 13. It can be seen that all samples are within an acceptable range. Four different compound studies were performed to verify the performance of the individual batches and the reproducibility in the compound performance indicators. The compound evaluation of the different batches confirmed that performance indicators were highly reproducible.

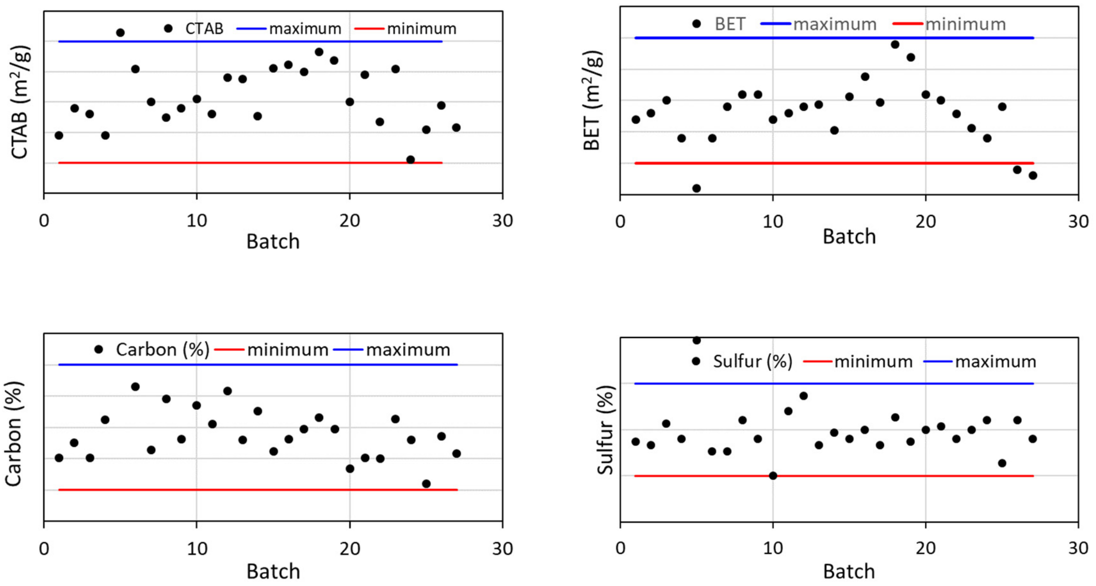


Figure 12. Characterization data of BXR-1006 pilot plant batches.

	Lowest value	Highest value
CTAB (m^2/g)	mean – 8%	Mean + 7%
BET (m^2/g)	mean – 6%	Mean + 6%
Carbon (%)	mean – 7%	Mean + 8%
Sulfur (%)	mean – 7%	Mean + 9%

Table 13. Batch variability of BXR-1006 pilot plant synthesis.

The silica produced was shipped to a re-packer to pack it in low-melt bags, prior to being shipped to BATO's tire plant. A specific SDS (safety data sheet) was generated for this treated silica prototype.

Subtask 7.2: Produce Novel Tread Compounds and Tires

Forty-five experimental tires with silica-filled treads and forty-five control tires with carbon black-filled treads were built for testing. Tires were needed to perform the same testing as in Task 4. Additionally, tires for a fuel efficiency test, which was not performed during Task 5, and twelve experimental tires and twelve control tires to be provided to the DOE for independent testing were built.

The rubber mixing and tire build was performed at BATO's Warren County tire plant in December 2017. A carbon black control tire tread compound (PT7207) was mixed and used to build tires. Two additional compounds, PT7607-1 and PT7607-2 were mixed for the silica compounds. The silica compound from the first mix (PT7607-1) was used for an extrusion trial, and the compound from the second mix was used to build the tires for testing. Table 14 shows the total mixing times, final mixing temperature and total consumed mixing energy for the three compounds. It can be seen that there was little variation among the three compounds. This shows that the study was performed without using additional mixing energy or temperature for the treated silica compounds. While optimization of the mixing procedure for the silica tread compounds can be a very useful tool to extract all the benefits from the silica compounds, it was the intention of this study to determine the benefits from using silica in place of carbon black, without influencing the results by the mixing procedure.

	Control PT7207	PT7607-1	PT7607-2
Total mixing time	100	104	106
Final mixing temperature	100	95	95
Total mixing energy	100	102	102

Table 14. Normalized mixing data from Warren County tire plant.

Task 8: On-Tire Testing

Lab compound data obtained at the Tire Plant is shown in Table 15. It can be seen that the compounds with the silica prototype have hardness, tear strength and lab wear indicator within 10% of the control, successfully achieving the goals of the project. Mooney viscosity is 23-27% higher, but this was expected and acceptable to the plant. Crosslink density (related to MH-ML) is higher which is also intentional due to the compound design previously determined. One finding was that the two silica compounds, which should have identical performance, provided different dynamic stiffness (E’) and hysteresis (tan δ). While the first compound used for the extrusion trial showed the expected improvement in hysteresis (tan δ reduced by 31%) at E’ similar to the control, the final compound used in the tire build showed 20% improvement in hysteresis and higher E’. The difference is also shown in Figure 13. It is hypothesized that the different results might be due to certain differences in dispersion between the two compounds, but this could not be confirmed. The second compound was used for the tire build, therefore some of the potential to improve fuel efficiency was lost.

Before performing tire tests, the tires needed to past certain endurance and high speed tests to guarantee their integrity on the road. The tires successfully passed all the requirements of these tests without any failure. Rolling resistance and fuel efficiency results are summarized in Table 16. The fuel efficiency test was performed according to SAE J1321 Type 2 Fuel Test at the Bridgestone Texas proving grounds. Control and silica tires were used in all truck positions (steer, drive and trailer). Temperature, ambient pressure, humidity and wind speed and direction were measured during the test. The 2.2% improvement in fuel efficiency falls short from the 4% goal set initially. Nevertheless, it is believed that if the silica compound from the first mix (PT7607-1) had been used instead, it is very possible that the 4% improvement in fuel efficiency might have been achieved. This is supported by the confirmation of the validity of the fuel efficiency indicators and the estimations made at the beginning of the project. When setting the goals, it was estimated that a 40% improvement in tan δ at 60°C would provide a 20%

improvement in rolling resistance and 4% improvement in fuel efficiency. The results obtained are consistent with this estimation. The 20% improvement in tan δ at 60°C provided a 7% improvement in rolling resistance and 2.2% improvement in fuel efficiency. The 31% improvement in tan δ at 60°C obtained by PT7607-1 in the extrusion trial, could have provided a 10.5% improvement in rolling resistance and 3.3% improvement in fuel efficiency. In the same way, the experimental tires produced during Task 5 using the BXR-990 silica prototype showed 47% improvement in tan δ at 60°C and 16% improvement in rolling resistance. Since this improvement in rolling resistance was more than double from the improvement in rolling resistance obtained in the final tire build, it is valid to estimate that the tire build with BXR-990 would have provided around a 5% improvement in fuel efficiency, should we have performed a fuel efficiency test.

	PT7207	PT7607-1	PT7607-2
ML(1+4)	100	127	123
MH-ML	100	119	125
T50	100	114	110
300% modulus	100	82	84
Elongation	100	106	103
Tensile strength	100	104	101
Tensile x elongation	100	110	104
Lab wear	**100**	**89**	**91**
Hardness	**100**	**98**	**97**
Dispersion (%)	100	98	97
Tear strength @ RT	**100**	**106**	**102**
Aged tear @ 100C	**100**	**91**	**91**
E'; 60C, 2%	100	103	118
Tan δ; 60C, 2%	100	69	80

Table 15. Normalized tire plant compound data.

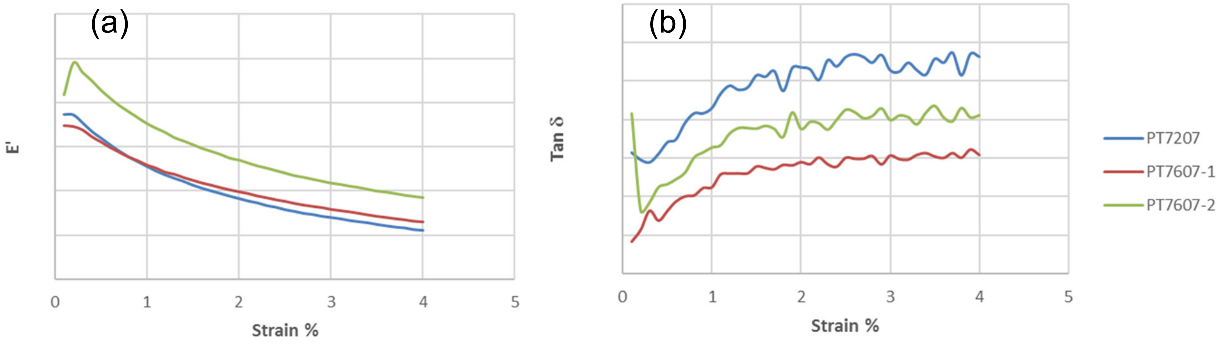


Figure 13. Strain sweep at 60°C. (a) E'; (b) tan δ.

The indoor wear rate test was performed on a drum with real-world modeled road surface plates. The inputs of the test include the test load, speed, and fore-aft and lateral forces (acceleration, braking, cornering), also modeled from real world inputs. Results from the wear test are shown in Figure 14. The projected miles for the tire with the silica tread are 31% lower than for the tire with the carbon black control tread. This shows that we were not able to significantly improve wear resistance. Other tools and further analysis of factors affecting wear are necessary to be evaluated to produce a silica tire with wear comparable to carbon black.

Test	CB control	PT7207-2
Rolling Resistance Coefficient (%)	100	93
Fuel consumption (%)	100	97.8

Table 16. Tire fuel efficiency results.

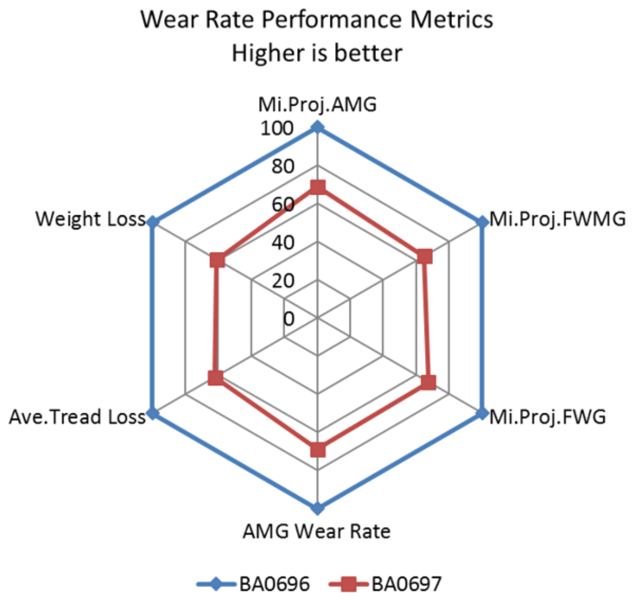


Figure 14. Tire wear results.

PROJECT CONCLUSIONS

During rubber mixing, distributing silica in the rubber matrix is a challenge. This is because silica has a very polar surface, while rubbers have little polarity. It was hypothesized that surface treatments could cover part of the surface by hydrophobic groups, and reduce the surface polarity, thus helping to wet the silica with rubber during mixing and improving silica dispersion. During the project, the effect of different silica surface treatments on the surface energy of silica were determined, and related to the silica dispersion in rubber compounds. The results demonstrated that reducing the surface energy of silica samples improved dispersion in rubber compounds. Also, the preference for silica to migrate to the different phases in polymer blends was determined. The studies performed in binary polymer blends showed that carbon black has a preference to distribute in the different polymer phases in the order: SBR>BR≈NR. Commercially available silica samples (treated and untreated) showed a preference in the order of SBR>NR>BR. Finally, the silica prototypes showed a preference in the order SBR=NR>BR.

The knowledge gained regarding dispersion of treated silicas in rubber compounds was used to perform a series of studies to develop a silica – rubber compound combination with optimum performance for TBR treads. Initially, two silica prototypes (BXR-990 and

BXR-991) were developed and used for a tire build at BATO's tire plant in Warren County, TN. Results were evaluated and further silica and compound optimization was performed, prior to a final tire build.

Manufacturing of the final silica prototype (BXR-1006) for the final tire build was performed at the PPG Silicas Pilot Plant in Monroeville, PA. Afterwards, experimental tires with silica-filled treads and control tires with carbon black-filled treads were built at BATO's Warren County tire plant.

The experimental TBR tires with silica-filled treads achieved the project goals for lab performance indicators, tread hardness and tear strength. The tires showed a 2.2% improvement in fuel efficiency compared to the control tires. While this improvement is lower than the 4% goal set initially, the improvement is significant and there are indicators that up to a 5% improvement in fuel efficiency could be achieved. This is supported by the confirmation of the validity of the fuel efficiency indicators made at the beginning of the project, and by the improvement in hysteresis and rolling resistance from tires built earlier in the project. The experimental tires produced using the BXR-990 silica prototype showed 47% improvement in tan δ at 60°C and 16% improvement in rolling resistance. Based on the results obtained, it is valid to estimate that the tires built with BXR-990 could provide around a 5% improvement in fuel efficiency, should we perform a fuel efficiency test.

Tire wear for the experimental tires was 31% worse than for the control tires with the carbon black-filled tread compound. Other tools and further analysis of factors affecting wear are necessary to be evaluated to produce a silica tire with wear comparable to carbon black.

Experimental and control tires were provided to the DOE for independent testing.

PUBLICATIONS, PRESENTATIONS AND AWARDS

- Presentation given at DOE Annual Merit Review; Washington, D.C; June 7th, 2016.
- Presentation given at DOE Annual Merit Review; Washington, D.C; June 7th, 2017.
- Presentation given at Tire Technology Expo; Hanover, Germany; February 22nd; 2018.
- Article written about the project in Tire Technology International magazine, March 2018 issue. http://ukimediaevents.com/publication/f04aa4ab/68
- Work selected as one of five finalists for the 2018 Tire Technology International, Environmental Achievement of the Year Award.
- Work selected as one of the finalists for the 2019 Tire Technology International, Tire Technology of the Year Award.

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