SPECIAL REPORT ——— Synthetic Rubber

Effect of polymer structure on compounded properties

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Both carbon black and silica are used as reinforcement agents in the manufacturing of tires. A significant degree of polymer-filler interaction is needed for these fillers to behave as a reinforcing agent instead of a non-reinforcing filler.

Unlike carbon black, typically silane coupling agents are needed with silica to achieve this level of interaction for styrene-butadiene rubbers.[1] The use of silica offers several advantages to performance versus only carbon black. One of the key performance improvements of silica is rolling resistance improvement, which can be predicted in the lab by a reduction in tan δ at 65°C.[2]

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Another key performance improvement is wet traction, which is typically predicted from an increase in the tan δ at 0°C.[3]

Additional data can be obtained by analysis of rheometric curves based on a fixed temperature with variable strain rates. This strain dependence of the storage modulus gives an indication of polymer-filler interaction, thanks to the Payne Effect.[4] Systems with reduced changes in storage modulus (G') values as the strain is increased, would indicate less filler-filler network breakdown, indicating better overall filler-polymer interaction.[5]

When exploring these effects, the method of polymerization can be very important. Styrene-butadiene rubber for tires can be made by both emulsion and solution polymerization techniques.

Anionic polymerization, which is typically carried out in a suitable hydrocarbon solvent, can behave as a living polymerization when the correct conditions are utilized. This living aspect of anionic polymerization allows for the addition of functional compounds, either during initiation or during termination.[6]

This functionalization can serve to increase the polymer-filler interaction for both carbon black, silica and mixed carbon black/silica systems. Another advantage of anionic polymerization is the ability to control the polymer microstructure, which in turn can alter the polymer glass transition temperature.[7]

The role of adding carbon black and/or silica functionalization to a polymer and the effects this has on compounded properties compared to a standard solution and emulsion polymer will be explored in this paper. This paper will discuss the effects this functionalization has on dynamic mechanical properties of these compounded blends.

An attempt to separate the benefits of polymer functionalization with a functionality able to react with filler from

Executive summary

The influence of rubber functionality on polymer-filler interaction was evaluated. The use of a polymer-containing silica functionality was shown to provide improved polymer-filler interaction, which also translated to projected increased wet traction and projected decreased rolling resistance based on RDA temperature sweep data. The addition of a silica functional polymer also was shown to allow for the reduction of silane levels without significant effect on properties.

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the effects of microstructure and molecular weight modification also will be made. Carbon black, carbon black/silica blends and mostly silica formulations, will be compared as part of this work.

Experimental

Materials

Four different rubber grades were used for this compounding evaluation. All polymers used for this evaluation are commercially available.

Polymer A is a cold polymerized emulsion styrene butadiene rubber. It has a styrene content of 24 percent, a Tg of -59°C, a polydispersivity index (PDI) of 3.99, and an ML4+1 of 59.2 MU.

Polymer B, is a solution polymerized styrene butadiene rubber. It has a styrene content of 23.1 percent, a Tg of -57°C, a PDI of 3.11, and an ML4+1 of 60.0 MU.

Polymer C, is a tin coupled, solution polymerized styrene butadiene rubber. It has a styrene content of 20.9 percent, a Tg of -26°C, a PDI of 1.61, and an ML4+1 of 70.5 MU.

Polymer D is a carbon black and silica functionalized solution polymerized styrene butadiene rubber. It has a styrene content of 24.5 percent, a Tg of -19°C, a PDI of 1.79, and an ML4+1 of 65.0 MU. None of the polymers utilized were oil extended. A summary of polymer properties can be found in **Table 1**.

The formulations used for this evaluation can be seen in **Tables 2-6**. A summary of raw materials used can also be seen in **Table 7**.

An all carbon black formulation based off ASTM D 3185-99 was evaluated. This formulation, Formulation 1, utilized industry reference Black 9 (IRB9),

with a full formulation summary contained in **Table 2**.[8]

A carbon black/silica blended formulation, referred to as Formulation 2, also was utilized. This carbon black/silica formulation was again based off the ASTM formulation with 49 percent of the carbon black replaced with silica. The silica utilized was Hi-Sil 190G from PPG industries Inc., which has an N_2 (BET-5) specific surface area of 195 m²/g (**Table 3**).

Formulation 3 is a mostly silica formulation, which was created by substituting silica for most of the carbon black in the formulation based off ASTM D 3185-99 mentioned above (**Table 4**). Formulation 3 contains 50 PHR silica and 7.5 PHR carbon black.

A high silica compound, Formulation 4, based off the work of Lin et al. also was utilized for comparisons (**Table 6**).[9] A variation of this high silica formulation also was mixed with variable levels of silane added to the silica/carbon black functional polymer, summarized in **Table 7**.

Process oil was added to Formulations 1, 2 and 3 to aid in processing of the samples. This was done to reduce the po-

Table 1: Summary of raw polymer properties.

Reference name	Polymer A	Polymer B	Polymer C	Polymer D
Cis[a], %	13.7	33.5	18.7	18.2
Trans[a], %	66.2	48.4	23.6	19.5
Vinyl[a], %	20.1	18.1	57.7	62.3
Styrene, %	24.0	23.1	20.9	24.5
T_g	-59.02	-56.92	-25.94	-19.09
Mn (kg/mol)	103.1	152.3	387.8	330.0
Mw (kg/mol)	411.2	473.8	624.7	588.9
Polydispersivity Index	3.99	3.11	1.61	1.79
ML4 4+1	52.9	60.0	70.5	65.0
T-80	21.4	15.7	3.9	4.1

[a] Cis, Trans, and Vinyl percent are based on butadiene composition only

Table 2: Carbon black formulation based off ASTM D3185-99.

Material	phr	Mixing stage of addition
Rubber	100	1st
IRB9	57.5	1st
Zinc Oxide	5	1st
Stearic Acid	2	1st
Oil	15	1st
Sulfur	1.75	3rd
Accelerator TBBS (NS)	1.15	3rd

Table 3: Mixed carbon black/silica formulation modified from ASTM D3185-99.

Material	phr	Mixing stage of addition
Rubber	100	1st
IRB9	29.5	1st
Hisil 190G	28	1st
Silane TESPD	2.8	1st
Zinc Oxide	5	1st
Stearic Acid	2	1st
Oil	15	1st
Sulfur	1.75	3rd
Accelerator TBBS (NS)	2	3rd
Accelerator DPG	2	3rd

Table 4: Mostly silica formulation modified from ASTM D3185-99 starting point.

Material	phr	Mixing stage of addition
Rubber	100	1st
IRB9	7.5	1st
Hisil 190G	50	1st
Silane TESPD	5	1st
Zinc Oxide	5	1st
Stearic Acid	2	1st
Oil	15	1st
Sulfur	1.75	3rd
Accelerator TBBS (NS)	1.3	3rd
Accelerator DPG	1.3	3rd

Table 5: High silica formulation used to evaluate the effect of silica functional polymer.

Material	phr	Mixing stage of addition
Evaluation rubber	70	1st
Natural Rubber (NR20)	15	1st
BR (EC140)	15	1st
Carbon Black (N-330)	10	1st
Silica (Hisil 190G)	80	1st
Silane TESPD	8	1st
6PPD	2	1st
Stearic Acid	2	1st
Wax	1.5	1st
Oil	31	1st
Zinc Oxide	2.5	3rd
Sulfur	0.75	3rd
Accelerator CBS	2	3rd
Accelerator DPG	2	3rd

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tential effects of higher viscosity with the higher silica loadings.[10,11] The carbon black and accelerator was increased per the ASTM D 3185-99 standard for varied oil level to account for this additional oil. When adding silica to Formulations 2 and 3, silane was added at an addition loading of 1:10 silane to silica. The silica surface can absorb curing accelerators resulting in significantly increased scorch times.[12]

To account for this accelerator absorption, additional accelerator and a co-accelerator, diphenyl guanidine (DPG), was added to Formulations 2 and 3.

Compound preparation

All compounds were mixed on a Farrel model BR Banbury lab mixer with a 1.6-liter chamber volume. Materials in Formulations 1-3 were mixed using a three-stage mix, with the final mix containing the curatives and dropping at a colder temperature to prevent the premature curing of the rubber compounds. An upside-down mixing method was employed for Formulations 1-3, to minimize powder losses and maintain consistency across the variable formulations. A breakdown of the stage each raw material was added for Formulations 1-3 can be found in **Tables 2-4**, respectively.

The material for the first mixing step was dropped at 160°C and was sheeted on a two-roll mill to cool and mass the material together in preparation for the secondary re-pass. The materials were then reprocessed through the Banbury mixer without additional materials being added. This secondary

mix was also processed to 160°C and then sheeted out on a two-roll mill.

For the third processing step the material from the previous step was added along with the curative package. This step was only mixed to 110°C to avoid any premature curing of the stock once the sulfur and accelerators were added. This material was again sheeted out on a two-roll mill in preparation for curing of the rubber material.

The mixing procedure used for Formulations 4 and 5 was designed to closely mirror the procedure used to mix the same formulations by Lin et. al. (**Table 8**). All materials were mixed at 70 RPM and sheeted out on a two-roll mill between each mixing stage.

Samples for Oscillating Die Rheometer and Mooney Viscosity were then removed from the raw mixture before curing. Materials were compression molded and cured using a Technical Machine Products Corp. (Cleveland) press. The press was electrically preheated to 160°C and then materials were compression molded and cured at 15.9 MPa for 20 minutes. Tensile specimens were cut out of a 15.24 cm by 15.24 cm by 0.19 cm plaque and pulled in parallel with the milling direction.

Samples for RDA and hardness were molded and cured in individual specimen molds. RDA samples were molded to 5.0 cm by 1.3 cm with a gap length of 3.3 cm. Samples were molded to 0.24 cm thickness for temperature sweep measurements and 0.62 cm thickness for strain sweep measurements.

Testing equipment, conditions

The molecular weight of the polymers was analyzed via gel permeation chromatography (GPC), also known as size exclusion chromatography (SEC). All testing was performed using a Tosoh EcoSEC HLC-8320 GPC (Tosoh Bioscience, Tokyo) with a Tosoh TSKgel guard column H XL-H 6.0 mm I.D. x 4 cm, 13μm (Tosoh Bioscience, King of Prussia, Pa.) in series with two Tosoh TSKgel GMHXL-L 7.8 mm I.D. x 30 cm, 9 μm columns (Tosoh Bioscience, King of Prussia). Analyte eluent was tetrahydrofuran (THF) stabilized with 0.025 percent butylated hydroxytoluene (Fisher Scientific, Fairlawn, N.J.).

Samples were prepared by dissolving 1 mg/mL polymer in THF. Samples were then filtered into 2 mL screw cap clear vials (Restek, Bellefonte, Pa.) using 0.45 μm PTFE syringe filters (Fisher Scientific, Fairlawn).

Samples were analyzed at a 120 μL injection volume with a flow of 1.00 mL/min (S pump) and 0.250 mL/min (R pump) of THF at a column temperature of 40°C for

a total run time of 23 minutes. Degasser was continually operational and both the UV (254 nm) and RI detectors were on during analysis. Results are expressed in molecular weight and polydispersity ratios, produced by RI detection.

The microstructure of the polymers was analyzed via Fourier transformed infrared spectroscopy (FTIR). Spectral peaks were observed at the following wavelengths: cis (3,004 cm^{-1}), trans (966 cm^{-1}), and vinyl (910 cm^{-1}) and in copolymers, styrene (3,026 cm^{-1}). All sample testing was performed using a Perkin Elmer Frontier FTIR (Perkin Elmer, Waltham, Mass.).

Samples were prepared by dissolving 0.3 mg of polymer in 10 mL carbon disulfide (CS$_2$, ACS grade, Fisher Scientific, Fairlawn). A background scan of air was measured, followed by a standard of known composition. The samples were then injected into a 0.02 cm path length KBr cell apparatus and scanned by the instrument. Results were calculated based on the spectral absorbancies of

Table 6: High silica formulation used for the evaluation of the effects of silane loading level.

Material	phr	Mixing stage of addition
Evaluation rubber	70	1st
Natural Rubber (NR20)	15	1st
BR (EC140)	15	1st
Carbon Black (N-330)	10	1st
Silica (Hisil 190G)	80	1st
	Varied from 8 to	
Silane TESPD	1.6	1st
6PPD	2	1st
Stearic Acid	2	1st
Wax	1.5	1st
Oil	31	1st
Zinc Oxide	2.5	3rd
Sulfur	0.75	3rd
Accelerator CBS	2	3rd
Accelerator DPG	2	3rd

Table 7: A summary of materials used for the compounding formulations in Tables 2-4.

Material	Manufacturer
IRB9 Carbon Black	Balentine enterprises
Zinc Oxide	Harwick Standard
Stearic Acid	Harwick Standard
Oil	(Hyprene BO125) Ergon Refining
Sulfur	Harwick Standard
Accelerator TBBS[a]	Harwick Standard
Silica - Hisil 190G	Harwick Standard
Silane – TESPD[b]	(SCA985) Struktol
Accelerator DPG[c]	MLPC International
NR20 (Natural Rubber)	HB Chemical Corporation
N339 Carbon Black	Continental Carbon
Santoflex 6PPD	Eastman Chemical
Wax	Sigma Aldrich
Santocure CBS[d]	Sovreign Chemical Company
BR - EC140[e]	Firestone Polymers

[a] TBBS = N-tert-butyl-2-benzothiazolesulfenamide

[b] TESPD = bis(triethoxysilylpropyl)disulfide

[c] DPG = diphenyl guanidine

[d] CBS = N-cyclohexyl-2-benzothiazole sulfenamide

[e] EC140 = high cis content BR rubber

Table 8: Mixing conditions used for the high silica formulations, Formulations 4 and 5.

Mixing stage	RPM	Mixing action
1st	70	Add polymer
1st	70	Mix for 40 seconds
1st	70	Add 1/2 silica and silane
1st	70	Mix for 50 seconds
1st	70	Add everything but carbon black and oil
1st	70	Mix for 60 seconds
1st	70	Add carbon black and oil
1st	70	Sweep at 150°C
1st	70	Drop at 160°C
2nd	75	Add 1st pass material
2nd	75	Drop at 160°C
3rd	50	Add 1st pass material
3rd	50	Add all other materials
3rd	50	Drop at 110°C

Table 9: Summary of compounding properties for Formulation 1, Table 1, a carbon black formula based off ASTM D3185-99.

Polymer evaluated	Polymer A	Polymer B	Polymer C	Polymer D
ML$_{1+4}$(100°C)	53	54	59	57
Tc10, min	8.94	8.68	10.31	10.57
Tc50, min	12.52	11.08	12.86	13.2
Tc90, min	18.08	13.71	16.82	16.67
ML, dNm	5.91	6.3	3.69	3.01
MH, dNm	36.96	38.53	37.84	33.2
MH − ML, dNm	31.05	32.23	34.15	30.19
Tensile strength, MPa	21.4	17.3	17.0	17.7
200% Modulus, MPa	7.2	6.0	8.6	8.5
Tensile elongation at Break, %	460	425	320	341
Shore A Hardness	56	54	53	55
Temperature Sweep				
Tan δ at 65°C	0.202	0.195	0.135	0.187
Tan δ at 0°C	0.303	0.256	0.504	0.517
Strain Sweep				
Δ G' at 65°C, MPa	1.59	1.14	0.16	0.29

Table 10: Summary of compounding properties for Formulation 2, Table 2, a carbon black/silica formula modified from ASTM D3185-99.

Polymer evaluated	Polymer A	Polymer B	Polymer C	Polymer D
ML$_{1+4}$(100°C)	57.7	64.39	70.76	57.3
Tc10, min	3.89	5.22	4.06	3.72
Tc50, min	4.99	6.62	5.07	4.67
Tc90, min	6.14	9.38	8.27	6.21
ML, dNm	5.82	4.2	4.89	4.38
MH, dNm	46.24	38.93	39.17	39.75
MH − ML, dNm	40.42	34.73	34.28	35.37
Tensile strength, MPa	14.369	15.463	17.477	18.572
200% Modulus, MPa	9.15	9.058	9.86	9.651
Tensile elongation at Break, %	278	305	313	339
Shore A Hardness	58	59	54	61
Temperature Sweep				
Tan δ at 65°C	0.177	0.141	0.112	0.122
Tan δ at 0°C	0.272	0.212	0.499	0.771
Strain Sweep				
Δ G' at 65°C, MPa	2.21	1.62	0.38	0.63

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Polymer

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the analyzed isomers using an internal computer macro program.[13]

Curing properties were characterized using an oscillating die rheometer (ODR 2000, Alpha Technologies, Hudson, Ohio) using a 24 minute method program at 160°C. The cure point at 10 percent (T10), 50 percent (T50), and 90 percent (T90) were observed and recorded. Minimum torque (ML) and maximum torque (MH) also were recorded. The T90 cure point was calculated using the MH.

Polymer Mooney Viscosity was determined on an Alpha Technologies Mooney Viscometer Model MV2000 by ASTM D-1646 at 100°C, with a time interval of 4 s and a rotor speed of 2 RPM.

The glass transition point was determined using a Perkin-Elmer Model DSC7 Calorimeter. Samples (15 mg) were heated from -125°C to 25°C at a rate of 10°C per minute and the glass transition temperature was determined by the instrument software.

Shore A hardness was determined on a Shore Instrument & Manufacturing Co. Model 716 durometer as described in ASTM D2240.

Torque and stress data were measured on a Rheometric Scientific Ares RDA instrument. Specimens were tested using a rectangular torsion fixture. Variable strain data was collected from 0-7 percent strain at 10.0 Hz and 65°C. Variable temperature data was collected from -100°C to -10°C at 10.0 Hz, 0.25 percent strain, and a rate of 2°C/min. From -10°C to 80°C the strain was increased to 2 percent and the rate of temperature increase was increased to 5°C/min.

Tensile testing was completed using an Instron 5900R Universal Testing Systems for tensile, compression, and flexure tests. Tests were completed using ASTM D-412, with Type C tensile bars.

Results and discussion

Analysis of Polymers A-D offers some insight into the differences between these polymers. All four polymers have similar styrene content with the entire range only representing a total difference of 3.6 percent. Even though these styrene contents are very similar, Polymer C and D both have significantly higher Tg representing an approximate increase of 36°C. This difference can be explained by the higher vinyl content of both Polymer C and D.[14]

Polymer C and D also have a much narrower PDI, when compared to Polymer A and B. It is known that Polymer C uses tin coupling, which would create an additional higher molecular weight peak due to the multiple chains coupling together.[15]

This is verified with a review of the actual GPC curves for Polymer C (**Fig. 1**). Polymer D, which contains both silica and carbon black functionality, can be shown to also contain this narrow molecular weight distribution and has the appearance of polymer coupling employed for this functionality (**Fig. 1**).

The overall results summary for Formulation 1, an all carbon black formulation, can be seen in **Table 9**. The Payne Effect can be used to explore the differences in polymer-filler interaction across different polymer and filler systems. In **Fig. 2**, the use of a carbon black or carbon black/silica functional polymer significantly decreases the change in G' over the strain range of 0-7 percent. This reduction of Δ G' indicates a reduction in filler-filler network is achieved using Polymer C and D.

This improvement in polymer-filler interaction can be shown to translate directly to changes in tan δ at both 0°C and 65°C, which are indications of wet traction and rolling resistance respectively (**Fig. 3**). Both the carbon black and carbon black/silica functional polymers had higher tan δ at 0°C, indicating better wet traction and also lower tan δ at 65°C, indicating reduced roll resistance when compared to an emulsion or solution polymer control.

The next formulation analyzed was a mixture of carbon black and silica, with the overall results from this study found in **Table 10**. The changes in G' with increasing strain can again be analyzed to understand the polymer-filler interaction differences in this mixed filler system (**Fig. 4**). There is a similar trend of the carbon black and carbon black/silica functional polymers exhibiting significantly improved polymer/filler interaction when compared to the nonfunctionalized polymers.

Polymers C and D again perform better in wet traction and rolling resistance predictors than Polymers A and B (**Fig. 5**). The key difference being that the silica/carbon black functional polymer now exhibits superior wet performance, with 54 percent higher tan δ at 0°C.

Formulation 3, the last in this series of experiments, replaced almost all the carbon black with silica with property results contained in **Table 11**. The G' versus shear rate curves show that the silica functional polymer now exhibits the best polymer-filler interaction (**Fig. 6**). This is again illustrated in the temperature sweep curves (**Fig. 7**).

With the higher silica formulation, we see the silica functional polymer outperforming the carbon black only functional polymer in both wet traction (89 percent improvement) and rolling resistance (20 percent reduction). Both functionalized polymers again are significantly better than the emulsion or solution non-functional polymers.

By using a similar formulation for these three comparisons, analysis of the effects of silica level on these polymers can then be completed. Silica has been added to tires as a carbon black replacement to improve wet traction and reduce roll resistance, but an understanding of how to optimize these benefits can be critical to achieving desired properties. When wet traction is plotted as a function of silica loading, only in the formulation utilizing the carbon black/silica functional polymer are these wet traction benefits realized (**Fig. 8**).

The tan δ at 0°C increased by 36 percent as the silica level was increased from 0 PHR to 50 PHR, indicating a significant improvement in wet traction as carbon black is replaced by silica for

Table 11: Summary of compounding properties for Formulation 3, Table 3, a mostly silica formula modified from ASTM D3185-99.

| Polymer evaluated	Polymer A	Polymer B	Polymer C	Polymer D
ML$_{1+4}$ (100°C)	73.8	72.7	103.0	95.6
Tc10, min	3.52	1.99	2.43	2.51
Tc50, min	6.02	3.16	4.21	4.55
Tc90, min	16.53	12.61	14.93	15.36
ML, dNm	7.6	8.4	10.1	8.8
MH, dNm	33.4	43.2	47.9	41.2
MH – ML, dNm	25.7	34.8	37.8	32.4
Tensile strength, MPa	19.7	15.0	12.1	11.6
200% Modulus, MPa	5.1	7.5	10.7	12.1
Tensile elongation at Break, %	515	327	216	193
Shore A Hardness	57	58	62	60
Temperature Sweep				
Tan δ at 65°C	0.194	0.156	0.102	0.080
Tan δ at 0°C	0.251	0.211	0.425	0.802
Strain Sweep				
Δ G' at 65°C, MPa	0.58	0.65	0.22	0.08

Table 12: Summary of compounding properties for Formulation 4, Table 4, a high silica formula.

Polymer evaluated	Polymer A	Polymer B	Polymer C	Polymer D
ML$_{1+4}$ (100°C)	59.9	61.3	58.4	61.6
Tc10, min	5.56	5.94	5.91	5.56
Tc50, min	7.27	7.95	8.12	8.06
Tc90, min	9.2	10.23	12.06	11.62
ML, dNm	7.59	8.13	6.7	6.57
MH, dNm	27.05	31.58	32.61	25.97
MH – ML, dNm	19.46	23.45	25.91	19.4
Tensile strength, MPa	16.2	12.6	14.9	12.9
200% Modulus, MPa	3.1	3.9	5.0	5.3
Tensile elongation at Break, %	680	509	493	401
Shore A Hardness	60	55	59	59
Temperature Sweep				
Tan δ at 65°C	0.268	0.262	0.223	0.178
Tan δ at 0°C	0.338	0.302	0.358	0.455
Strain Sweep				
Δ G' at 65°C, MPa	4.19	4.15	1.98	0.73

Table 13: Summary of compounding properties for Formulation 5, Table 5, a high silica formula with the silane level varied.

Polymer evaluated	8 phr silane	6.4 phr silane	4.8 phr silane	3.2 phr silane	1.6 phr silane
ML$_{1+4}$ (100°C)	69.6	72.6	84.2	89.6	118.0
Tc10, min	5.99	6.19	4.7	3.67	2.41
Tc50, min	7.86	8.44	7.06	6.12	3.75
Tc90, min	10.85	11.51	11.21	12.79	10.11
ML, dNm	9.26	9.41	10.85	12.42	17.95
MH, dNm	35.09	32.48	31.16	31	47.11
MH – ML, dNm	25.83	23.07	20.31	18.58	29.16
Tensile strength, MPa	14.1	13.5	13.7	13.0	9.2
200% Modulus, MPa	4.4	3.9	3.5	2.6	2.6
Tensile elongation at Break, %	491	524	602	717	689
Shore A Hardness	55	58	56	59	58
Temperature Sweep					
Tan δ at 65°C	0.195	0.199	0.212	0.206	0.184
Tan δ at 0°C	0.413	0.414	0.408	0.395	0.308
Strain Sweep					
Δ G' at 65°C, MPa	1.82	1.93	1.83	1.87	4.03

Fig. 1: GPC curves for the four polymers analyzed in this paper.
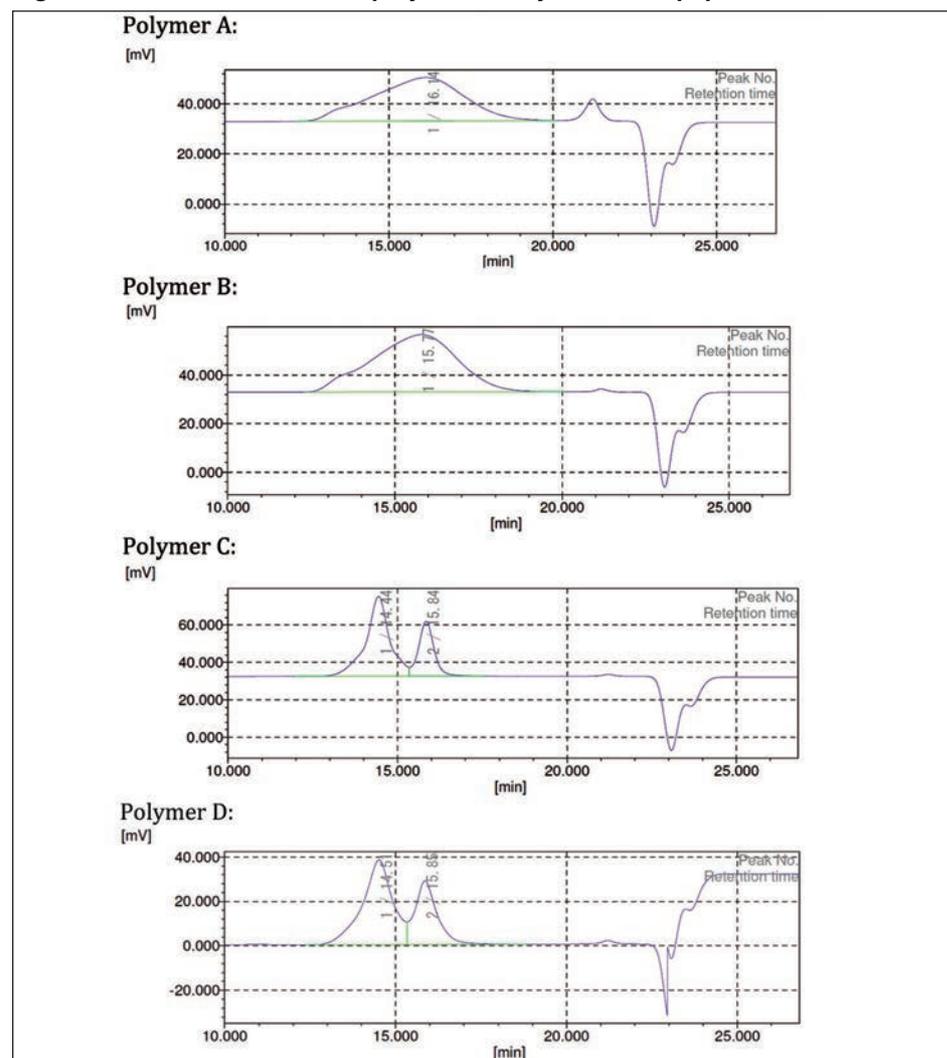
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this polymer formulation. A similar trend is observed when we compare silica loading levels for each of the polymer systems at 65°C as well (**Fig. 9**). The overall rolling resistance is decreased with the replacement of carbon black with silica, but a much more significant and steady decrease is seen in the system utilizing the carbon black/silica functional polymer.

The tan δ at 65°C decreased by 65 percent as the silica loading was increased from 0 PHR to 50 PHR. The addition of silane to the system improves the overall polymer-filler interaction, as can be seen by the overall decrease in Δ G' at higher silica loading levels (**Fig. 10**). This data illustrates that additional benefits are observed using a silica functional polymer beyond the benefits realized by a silane functionalizing agent.

The review of this data shows some interesting trends, but is all done in formulations based on ASTM 3185-99 and utilizing a single polymer system. Analysis can instead be done based on a

more complete compounding formula such as the high silica formula used for silane analysis by Lin, et. al. The overall property results summary for this work are contained in **Table 12**.

A much clearer view of the differences in these polymer systems can be seen from the strain sweeps for these materials at 65°C (**Fig. 11**). The same trends apply as in the previous high silica formulation, with the carbon black/silane functionalized material exhibiting significantly better polymer filler interaction as indicated by a 63 percent reduction in Δ G' at 65°C versus the carbon black functionalized material. Since these polymers have similar microstructure, Tg, and molecular weight profiles, the benefits can be attributed to the addition of functionalization targeted to interact with the silica. The carbon black functionalized material was still better than the nonfunctional solution or emulsion formulations, again agreeing with the previous data.

This information is further reinforced

by the improved wet traction and reduced rolling resistance also exhibited by the carbon black/silica functionalized material (**Fig. 12**). A 33 percent reduction in tan δ at 65°C is observed with the use of a carbon black/silica functional rubber instead of a carbon black functional only. A 21 percent increase in tan δ at 0°C also is seen using a silica/carbon black functional polymer. This further illustrates the advantages of utilizing a polymer containing silica functionality over a similarly structured polymer containing only carbon black functionality.

It can be seen in the previous example that the silica functional polymer is interacting with the silica in a way that increases the polymer-filler interaction. Silane is typically added to a compound mixture to improve the silica polymer interaction. Addition of silane can add cost to a compound formulation, so it is of interest to understand and optimize this level when using a polymer that already contains silica functionality.

Silica to silane ratios in the range from

10:1 to 50:1 were explored utilizing the silica/carbon black functionalized polymer with overall results contained in **Table 13**. A review of Δ G' compared to silane loading, shows very similar values until the silane is decreased to a point below 40 percent of the original value (**Fig. 13**). Between the 25:1 and 50:1 silica to silane ratios a significant decrease in polymer-filler interaction can be seen for these silica functional polymers, indicating the ability to use reduced silane levels, but also the need for some level of silane to optimize properties.

This data is further reinforced by the temperature curves, which also show very little change in the curves until the silane is dropped to 20 percent of the original level (**Fig. 14**). Use of a 25:1 silica to silane ratio in a silica functionalized polymer, still exhibits a 10 percent improvement in tan δ at 0°C and an 8 percent decrease in tan δ at 65°C, when compared to a carbon black functional only polymer using a 10:1 silica to silane ratio.

Fig. 2: Strain sweep from 0 percent to 7 percent strain for carbon black formulas utilizing ASTM D3185-99.
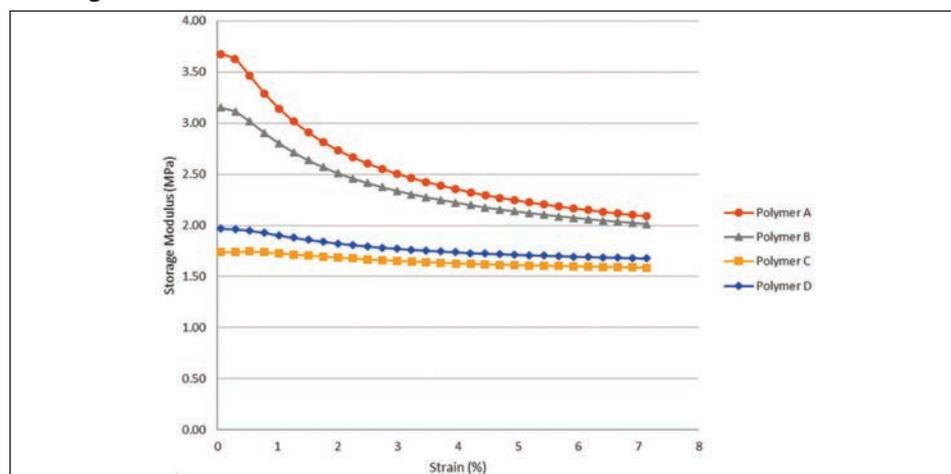

Fig. 3: Temperature sweep from -100°C to 80°C for carbon black formulas utilizing ASTM D3185-99.
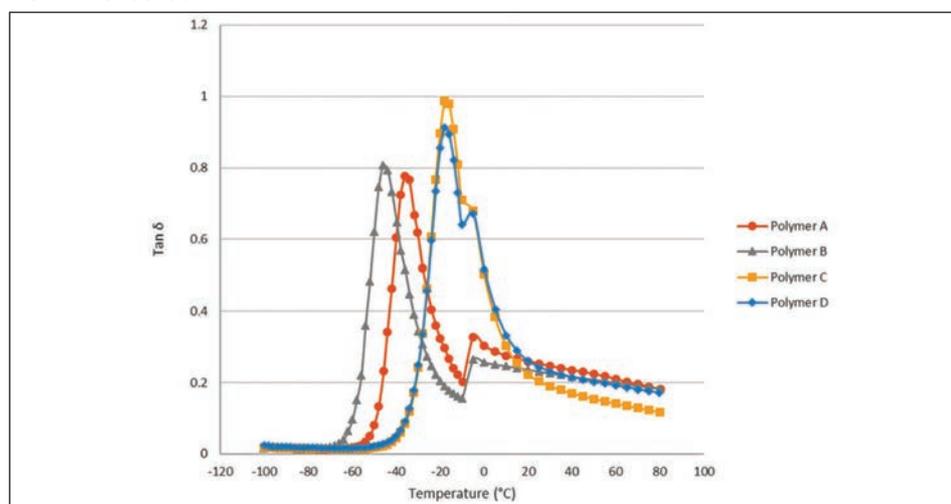

Fig. 4: Strain sweep from 0 percent to 7 percent strain for silica/carbon black formulas utilizing ASTM D3185-99.
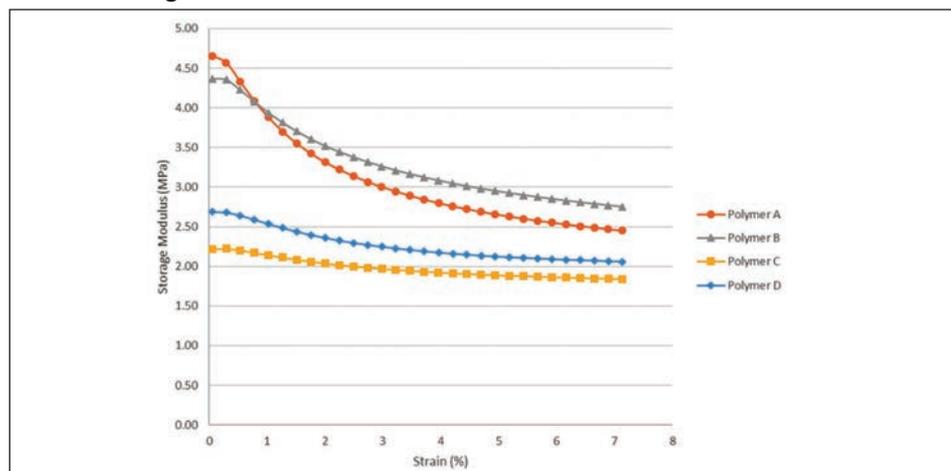

Fig. 5: Temperature sweep from -100°C to 80°C for silica/carbon black formulas utilizing ASTM D3185-99.
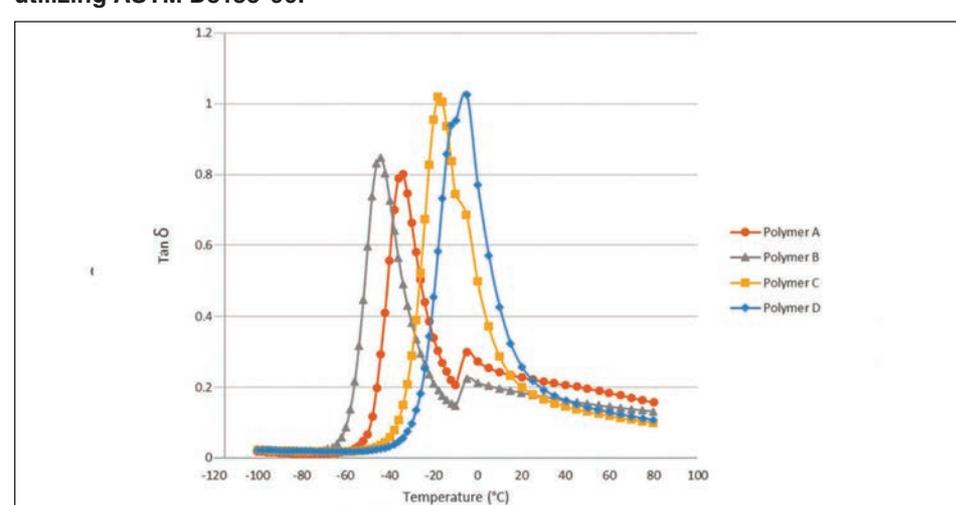

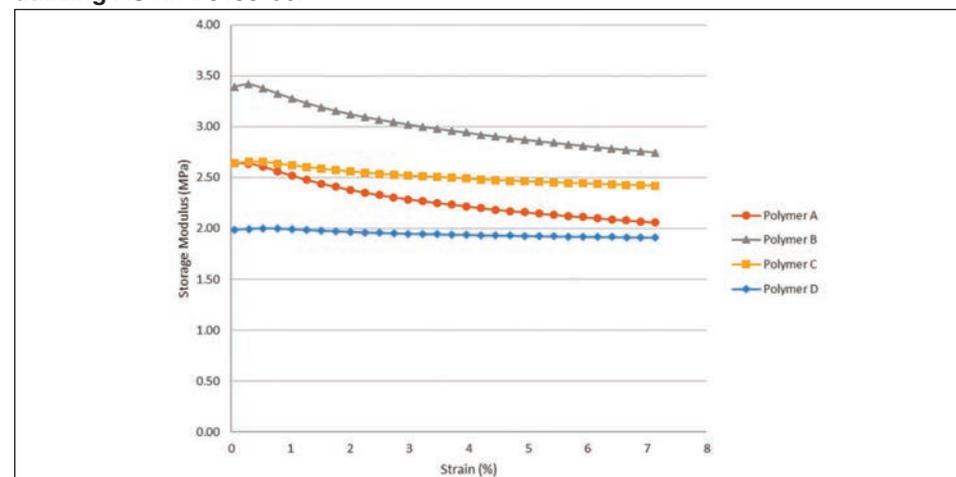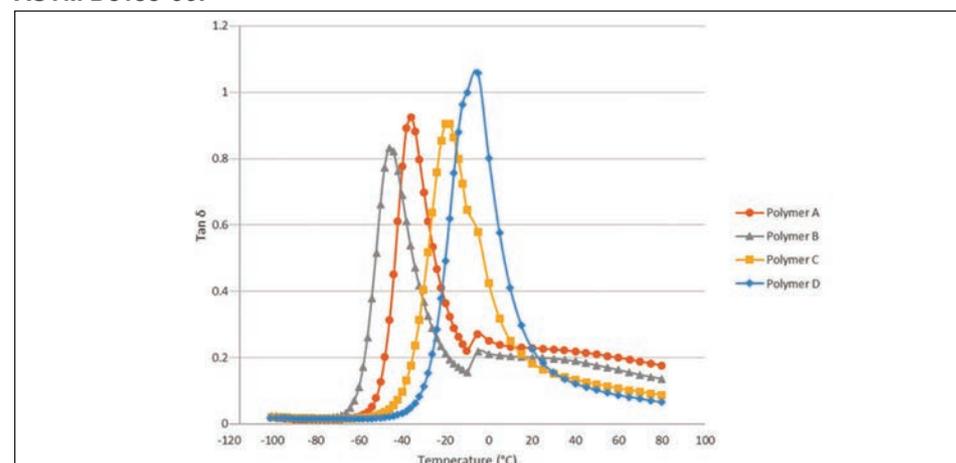**Fig. 6: Strain sweep from 0 percent to 7 percent strain for mostly silica formulas utilizing ASTM D3185-99.**

Fig. 7: Temperature sweep from -100°C to 80°C for mostly silica formulas utilizing ASTM D3185-99.

SPECIAL REPORT

Synthetic Rubber

Polymer

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Conclusions

Compounds using carbon black, carbon black/silica, and mostly silica were prepared along with a high silica formulation with specific analysis focused on polymer-filler interaction and the effects on both wet traction and roll resistance.

The addition of rubber functionalized for the specific filler system used can offer benefits in both lower roll resistance and increased wet traction.

Using a polymer with silica functionality provides a 33 percent reduction of tan δ at 65°C over a similarly structured polymer with only carbon black functionality when used in a high silica formulation. A 21 percent increase in tan δ at 0°C also is observed using a silica functional polymer in this same formulation.

Use of a silica functional polymer achieved superior wet traction and roll resistance results compared to a similar structure carbon black only functional polymer even with silane levels reduced from 10:1 down to 25:1 silica to silane PHR ratio.

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Fig. 11: Strain sweep from 0 percent to 7 percent strain for a high silica formula.
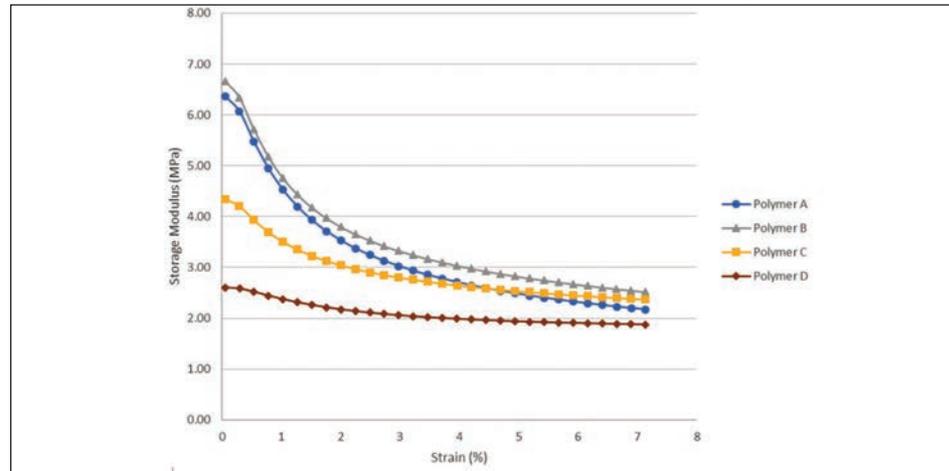
Fig. 12: Temperature sweep from -100°C to 80°C for a high silica formula.

Fig. 13: Effects of silane loading level on storage modulus for a high silica formulation using a silica functional polymer.

Fig. 14: Effects of silane loading level on temperature sweep data for a high silica formulation using a silica functional polymer.
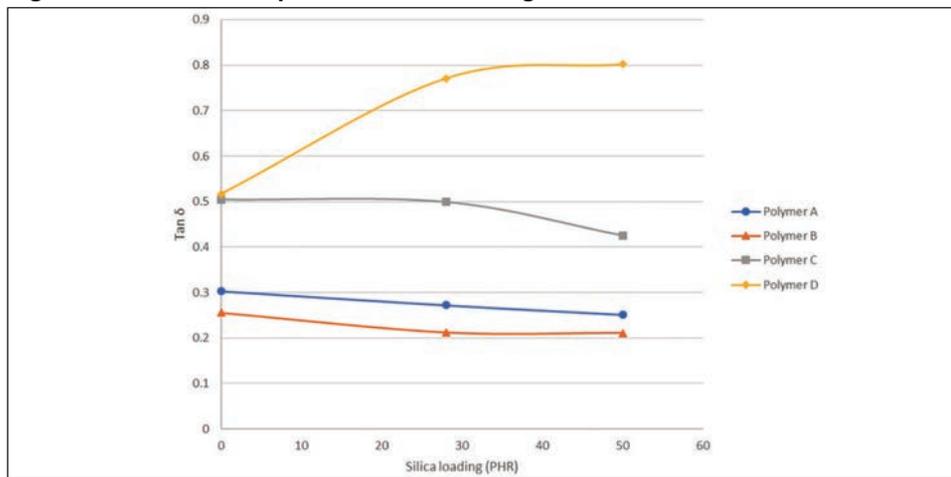

Fig. 8: Tan δ at 0°C compared to silica loading.

Fig. 9: Tan δ at 65°C compared to silica loading.

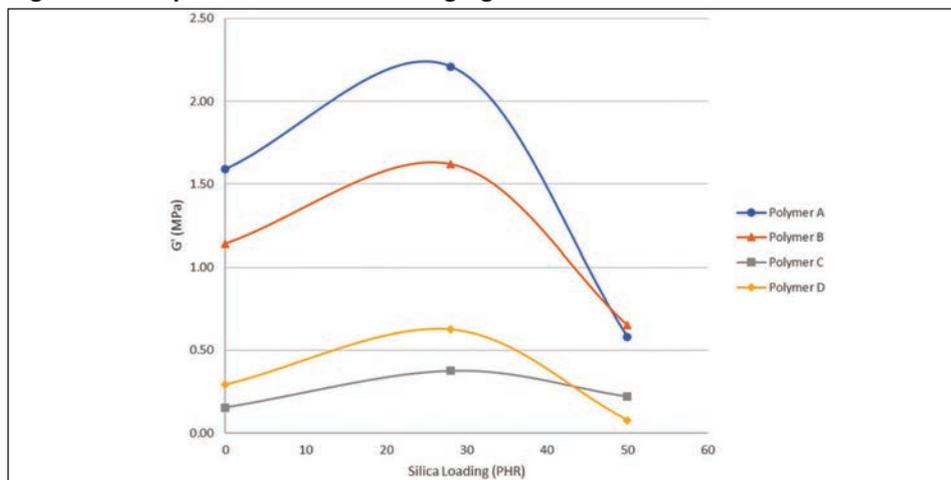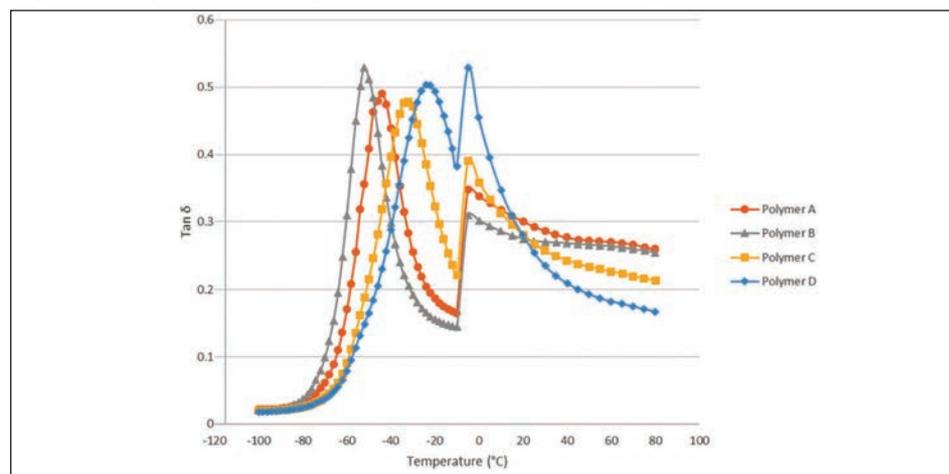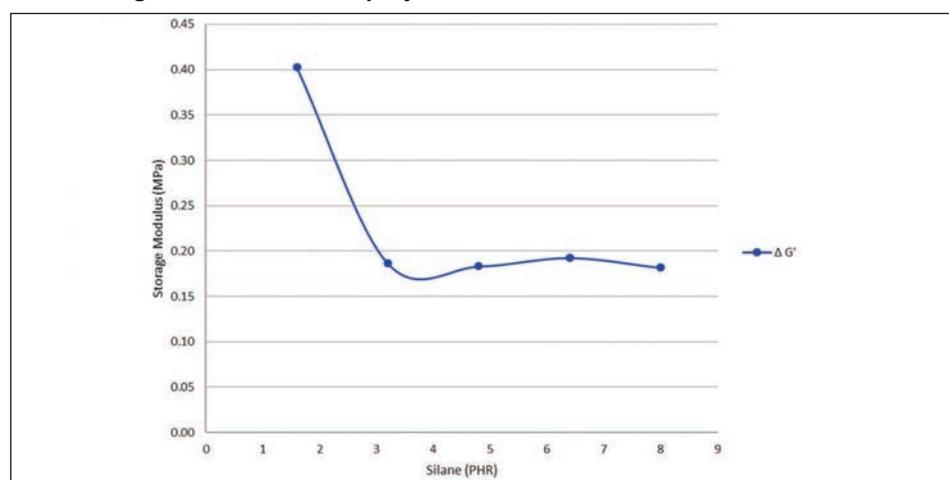**Fig. 10: A comparison of G' with changing silica levels for Formulations 1-3.**