Sustainable Nzerosil silicas from renewable rice husk

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Executive summary

Precipitated silica used in passenger car radial (PCR) tire treads desirably stretches the magic triangle by increasing wet traction, decreasing rolling resistance and maintaining wear, thus creating the green tire. OSC manufactures the highly-reinforcing Tokusil-brand 255EG in an easily dispersible granulated form, and the highly dispersible Eecosil-brand 350MG (BET N2 surface area ~170 m²/g) microgranule from sodium silicate made from sand (crystalline quartz). Recycling in silica manufacture is promoted by using cullet (crushed glass) or off-grade silicas generated during product changes to form the sodium silicate starting material. Silica synthesis proceeds by following the same production steps of controlled acid neutralization of silicate to form amorphous silicas.

The next generation of reinforcing silicas is the sustainable Nzerosil-brand net zero emission series made from the bio-renewable rice husk agricultural waste. Silica properties and key property performance in a model PCR tire tread were shown to be equivalent to commercial silicas. Tires for ultra-high performance passenger, electric vehicle and light truck tires require increased capabilities. Thus, the present study quantifies the performance of the high surface area (BET ~210 m²/g) Nzerosil RH-230G granulated silica made from rice husk compared to Eecosil 230G granules, Eecosil 230MG microgranules and a commercial competitor in a 100-phr silica model tire tread. Compound cure, physical and viscoelastic properties and silica dispersion are measured.

Results showed the performance of sustainable Nzerosil RH-230G is equivalent within ~10 percent to that of the granulated Eecosil 230G and microgranular Eecosil 230MG silicas made from glass cullet, and performance is slightly improved versus Silica 1, the commercial competitor product. A 5-pass mixing sequence with a simple remill step is needed to disperse silica to reduce percent-white areas and maximize the M300/M100 reinforcement index.

Introduction

Michelin[1] developed a passenger car (PCR) tire tread formulation using a solution-polymerized SBR/high cis-BR elastomer blend and a highly dispersible silica[2] (HDS) that increased wet traction, reduced rolling resistance and maintained wear life compared to carbon black or conventional silica controls. Multiple thermomechanical mixing steps were used to disperse silica and to react with a bi-functional organosilane in order to maximize the M300/M100 reinforcement index. The silica-filled tread with improved performance became known as the green tire.

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OSC Group

Diamond Silica was founded in 1978, and five years later renamed PPG Industries Taiwan after a joint venture agreement to manufacture HiSil-brand amorphous precipitated silicas. In 2003, Oriental Silicas Corp.[3] was created by purchasing all PPG silica businesses in Asia, including plants in Thailand and China. The next year via an investment by Tokoyama Corp., the joint venture made the highly reinforcing Tokusil-brand easily dispersing silicas in granulated form. In 2011, OSC purchased Tokoyama's silica businesses, including their Thailand plant, and created Oriental Silica Siam Corp. for the two Thailand silica factories.

Silicon dioxide

The Earth's crust is continental (20-80 km) and oceanic (7-12 km) layers of mostly igneous rock containing ~90 percent silicate minerals. Silicon dioxide (SiO_2) is ~26 percent by weight, with about one-half found as inert, abrasive large particles in the form of crystalline quartz, cristobalite and tridymite.[4] Small quantities of other elements are present including aluminum, calcium, iron, magnesium, potassium, sodium and titanium. Diatomaceous earth (dolomite) found in sedimentary rocks is an amorphous silica containing up to 30 percent organic matter and inorganic impurities such as clay and soluble salts.

Silica manufacture

Since exposure of workers to respirable crystalline silica is associated with elevated rates of lung cancer,[5] crystalline sand is not directly used in rubber products. Rather it is the starting material in the manufacture of amorphous precipitated silica summarized by two general chemical reactions: (1) formation of sodium silicate [$(SiO_2)Na_2O$] by reacting crystalline sand (SiO_2) with soda ash (Na_2CO_3) in a furnace, called the dry process, followed by (2) controlled acid neutralization of the silicate to synthesize amorphous precipitated silicas.

Manufacturing steps are much more complicated.[6] Exact reaction conditions can vary and are proprietary, but generally include reactor size, batch fill volume, sodium silicate concentration, acid type and strength, solution pH, silicate and acid addition rates, stirring efficiency, reaction temperature and time, and quenching rate in order to form amorphous precipitated silica with targeted desirable properties .

Recycling in silica manufacture

Cullet (crushed glass) recycled from various broken/discarded sources can be the starting material by reacting with soda ash in an autoclave, called a wet solution process to form sodium silicate (**Fig. 2**). This step is followed by the same acid neutralization reaction to synthesize targeted amorphous precipitated silicas (**Fig. 1.2**).

Silicas made during product grade changes or plant interruptions due to scheduled maintenance or power outages, etc., can also be recycled. For example, OSC produces silicas for various non-rubber applications,[3] including:

- thickening and abrasion for polishing and dental applications;
- matting, thickening and de-

Fig. 1: Silica manufacturing of (1) silicate production via the dry furnace process of natural minerals (crystalline quartz sand), followed by (2) controlled acid neutralization to synthesize amorphous precipitated silica.

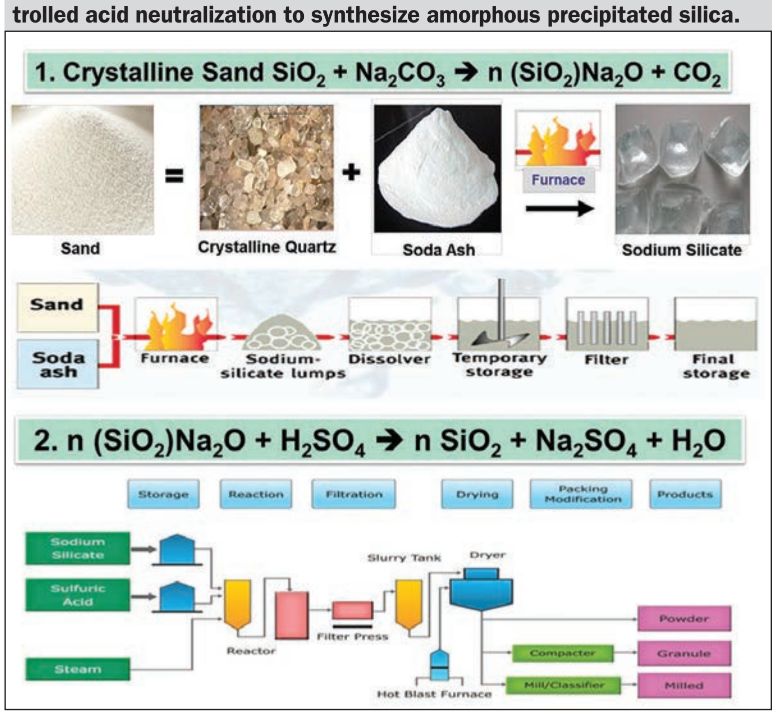


Fig. 2: Silica manufacturing of (1) silicate production via the wet autoclave process starting with cullet (crushed recycled glass), followed by (2) controlled acid neutralization to synthesize amorphous precipitated silica.

Fig. 3: Granulated silica (left) obtained by drying, milling into a powder and compacting on a textured 2-roll mill, and microgranular silica (right) obtained by direct spray drying to the desired particle size.

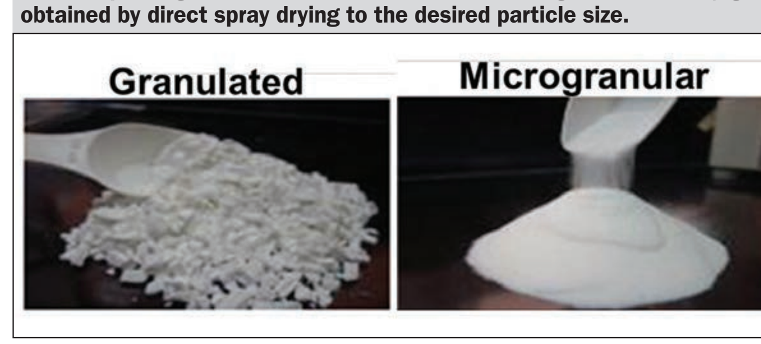


Fig. 4: Plants that yield a high ash content and high amount of silica in the ash.

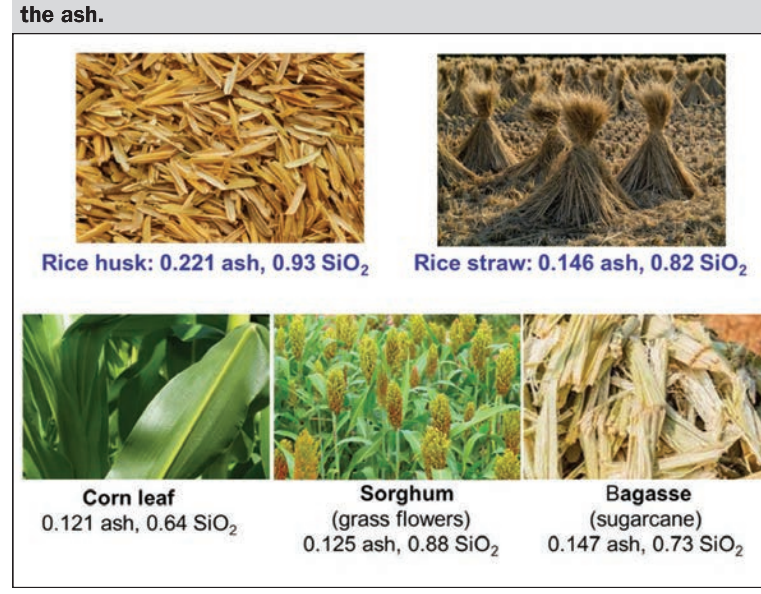
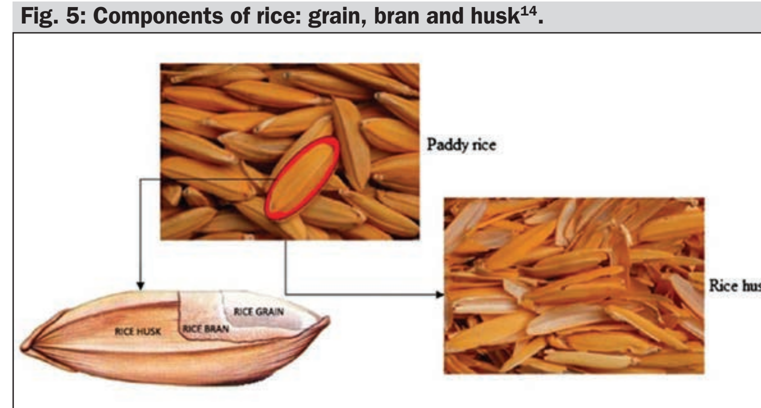


Fig. 5: Components of rice: grain, bran and husk[14].



foaming in coatings, adhesives and sealants; and

• carrier and free-flow in feedstuffs, animal feeds and pharmaceuticals.

Manufacturing plants were established by OSC in 2013 in Taiwan and in 2021 in Malaysia to produce sodium silicate from glass cullet.[3]

Reinforcing precipitated silicas for PCR tires produced from glass cullet are: easily dispersing Tokusil-brand 255EG silica in a granulated (milled/compacted) form, and the highly dispersible Eecosil-brand 350MG silica[7-10] in a dust-free microgranular form (BET N_2 surface area ~170 m^2/g) (**Fig. 3**).

Sustainability in silica manufacture

The Oxford dictionary provides one definition of sustainability as "avoiding the depletion of natural resources in order to maintain an ecological balance." The tire industry desires replacement of oil-derived materials with sustainable products derived from renewable biomass: polymers, reinforcing fillers, fiber reinforcements, and process and performance aids.

Silica can be directly obtained from a variety of eco-friendly renewable bio-origin sources. Rice husk (yield index = 20.5), rice straw (12.0), cornflower (11.1),

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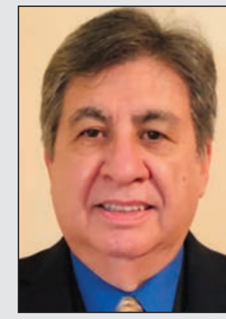

Waddell

The authors

Tim Yu-Ting Lin is president of Oriental Silicas Corp.. For 20-plus years, he has been assistant to the president, planning director and worked on various marketing, R&D and environment, health and safety projects. Lin has a BBA from National Taiwan University, a master's of business administration from National Sun Yatsen University (Taiwan), and previously worked at Tokuyama Corp. in Japan.

Spencer Lee is vice president of marketing, responsible for the global precipitated silica and vulcanized vegetable oil businesses. He has a bachelor's in chemistry from National Chung-Hsing University (Taiwan) and has about 50 years of experience in the rubber, plastics and silica industries. He joined PPG-Taiwan in 1986, and previously held leadership positions in sales and in technology.

Chris Wu is manager, R&D, responsible for new expansion projects at all OSC manufacturing sites in Asia. He has a master's from the University of Massachusetts, and worked at OSC for more than 25 years. Wu is responsible for university collaborations for industrial technology development and small business innovation research programs He led the development of highly dispersible Eecosil-brand and sustainable Nzerosil-brand rice husk silica technologies.

Danniel Liao is supervisor, product application and development, and has a bachelor's from National Chi Nan University (Taiwan) and a master's in chemistry from National Chung Hsing University (Taiwan). He worked as a research compound engineer at Cheng Shin Tire, and joined OSC six years ago focusing on high surface area Eecosil and sustainable Nzerosil rice husk silica applications.

Anthony Lin is engineer, product application and development, has a bachelor's in pharmacy from National Taiwan University (Taiwan) and worked as a pharmacist in their University Hospital. He joined OSC three years ago focusing on extraction of silica from renewable biomaterials, purification of ash residues and sustainable Nzerosil from rice husk.

Walter Waddell is a senior technology consultant. He has a bachelor's and doctorate in chemistry, 37 patents, more than 160 publications and over 180 presentations. Waddell has received awards from the American Chemical Society, ACS Rubber Division, International Rubber Conference and *Rubber & Plastics News.* He retired from ExxonMobil after previously working at Carnegie-Mellon University, Goodyear and PPG.

Fig. 6: Silica manufacturing of (1) silicate production via a furnace process to ash rice husk followed by a wet autoclave process, followed by (2) controlled acid neutralization to synthesize amorphous precipitated silica.

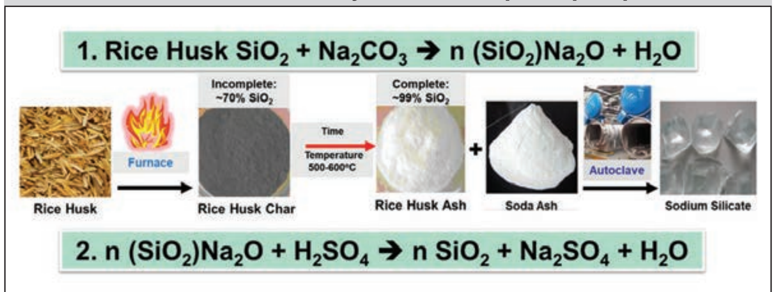


Table 1: Model 100-phr silica-filled tire tread formula with 4-pass mix sequence.

Mix Pass	Ingredient	phr
1st	SSBR, Trinseo 4602	75
	cis-BR, TSR 0150	25
	Silica, Eecosil 230MG	80
	TESPD Coupling Agent, Evonik Si75	10
	Carbon Black, N234	3
	Process Oil, TDAE	33.1
2nd	Silica, Eecosil 230MG	20
	Process Oil, TDAE	10
3rd	Microcrystalline Wax	1.5
	Activator, Zinc Oxide	2.5
	Accelerator, DPG	2.7
4th	Stearic acid	2
	Sulfur	1.1
	Accelerator, CBS	2.4

Fig. 7: Four mix sequences of model tread formula shown in Table 1.

Mix Stage	4-Pass	5-Pass	5-Pass	6-Pass
1st	Polymers/Silica /Silane/Oil	Polymers/Silica /Silane/Oil	Polymers/Silica /Silane/Oil	Polymers/Silica /Silane/Oil
2nd	Silica/Oil	Silica/Oil	Silica/Oil	Silica/Oil
3rd	Chemicals	*REMILL*	Chemicals	*REMILL #1*
4th	Productive Mix	Chemicals	*REMILL*	Chemicals
5th		Productive Mix	Productive mix	*REMILL #2*
6th				Productive Mix

Table 2: Key process, physical and viscoelastic test results of four mix sequences.

Mixing Sequence	4-Pass, No Remill	5-Pass, Stage 3 Remill	5-Pass, Stage 4 Remill	6-Pass, 2 Remills
MH-ML (dNm)	8.9	8.2	7.5	7.7
Ts1 (min)	2.4	2.2	2.6	2.3
T90 (min)	9.4	9.4	9.4	10
Tensile Strength (MPa)	9.1	7.9	8.5	7.7
Elongation at Break (%)	281	235	290	206
M100 (MPa)	2.7	2.8	2.2	3.2
M200 (MPa)	5.9	6.4	5.0	7.5
Reinforcement Index (M200/M100)	2.19	2.29	2.27	2.34
Wet Traction (tan δ 0)	0.379	0.390	0.389	0.399
Rolling Resistance (tan δ 60)	0.145	0.137	0.140	0.137

Fig. 8: Graph of %-white areas from ImageJ analysis of SEM@100X of four mix sequences.

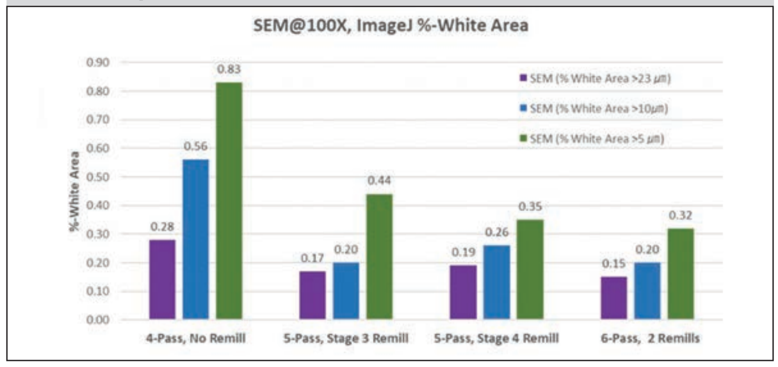
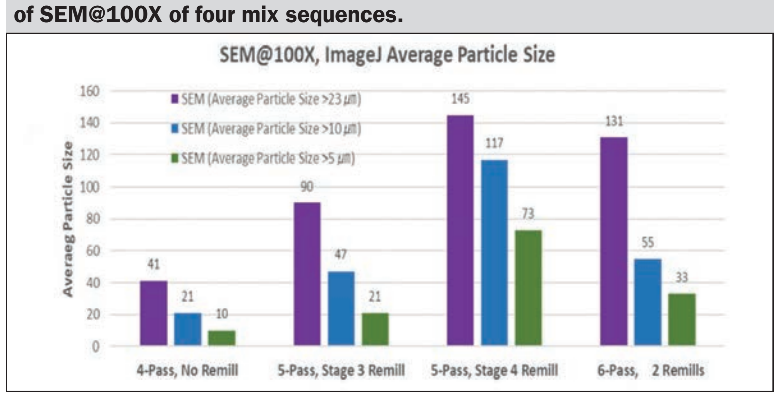


Fig. 9: Graph of average particle size distributions from imageJ analysis of SEM@100X of four mix sequences.



Nzerosil

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sorghum (grass flowers, 10.7), and bagasse (sugar cane, 9.5) give the highest index obtained by multiplying the ash content of the plant by the silica content in the ash[11] (**Fig. 4**). X-ray fluorescence identified other elements in rice husk ash including aluminum, calcium, iron, magnesium, manganese, phosphorus, potassium, sodium and sulfur.[12]

Rice husk is the second most consumed food source globally after corn (index = 7.8); however, corn byproducts already have commercial applications, for example ethanol in gasoline to form gasohol. In 2022, 776.5 million metric tons of rice were produced worldwide, with 12 countries producing >10 mmt. All countries except for #11 Brazil are located in Asia.[13]

Rice husk is the outermost layer of the rice grain (**Fig. 5**). Milling yields ~70 percent rice, ~20 percent husk, 8 percent bran and 2 percent germ.[14] People consume the white rice grain and the brown rice, which contains the bran and germ. An agricultural waste byproduct of milling, the husk was simply burnt in an open-air field as a fuel or dumped into a landfill, with both actions having potentially detrimental environmental effects. Currently, rice husk ash can be used as a raw material for manufacturing industrial chemicals (silicates, zeolites, catalysts, nanocomposites), in building material additives (steel industry, concrete, cement), in lightweight construction materials (insulators, adsorbents, activated carbon), as soil conditioners (fertilizer) and as alternative fuel for energy.[15-16]

Rice husk is the current biosource of choice of silicate for sustainable silica manufacture (**Fig. 6**).

Sustainable Nzerosil series

Sustainable Nzerosil-brand silicas from renewable rice husk were developed to match current rubber reinforcing silicas: Nzerosil RH-255EG granulated silica (BET N_2 surface area ~170 m^2/g) is equivalent to Tokusil 255EG, Nzerosil RH-350MG (BET ~170 m2/g) microgranular silica is equivalent to Eecosil 350MG, and high surface area Nzerosil RH-230G granulated silica (BET ~210 m^2/g) is equivalent to Eecosil 230G granules based on compound cure, physical and viscoelastic performance, and silica dispersion in model passenger car tire treads.[18]

The present study is research on sustainable high surface area Nzerosil RH-230G granules from renewable rice husk compared to Eecosil 230G granules, Eecosil 230MG microgranules[17] and a commercial competitor product in a 100-phr silica model tread for ultra=high performance car, electric vehicle and light truck tires.

Experimental

All compounding was performed in a Kobelco BB-2 1.5L mixer with 4-Wing H tangential

Table 3: Model 100-phr silica-filled tire tread formula with varying levels of zinc process aid with 5-pass mix sequence.

	Tread Compound	A	B	C
Mix Pass	Ingredient	phr	phr	phr
1st	SSBR, Trinseo 4602	75	75	75
	cis-BR, TSR 0150	25	25	25
	Silica, Eecosil 230MG	80	80	80
	TESPD Coupling Agent, Evonik Si75	10	10	8
	Carbon Black, N234	3	3	3
	Process Oil, TDAE	33.1	33.1	33.1
	Process Aid, Struktol EF-44	0	2	6
2nd	Silica, Eecosil 230MG	20	20	20
	Process Oil, TDAE	10	10	10
3rd	REMILL			
4th	Microcrystalline Wax	1.5	1.5	1.5
	Activator, Zinc Oxide	2.5	1	2.5
	Accelerator, DPG	2.7	1.8	1.8
5th	Stearic acid	2	1	1
	Sulfur	1.1	1.25	1.1
	Accelerator, CBS	2.4	1.5	1.5

Table 4: Key process, physical and viscoelastic test results with varying levels of zinc process aid.

Tread Compound	A	B	C
MH-ML (dNm)	8.2	7.1	5.44
Ts1 (min)	2.2	2.5	4.2
T90 (min)	9.4	10.9	13.6
Tensile Strength (MPa)	7.9	11.2	7.4
Elongation at Break (%)	235	314	334
M100 (MPa)	2.8	2.6	2.1
M200 (MPa)	6.4	6.0	4.1
M200/M100 Index	2.3	2.3	2.0
M300 (MPa)		10.3	6.5
M300/M100 Index		4.00	3.1
Wet Traction (tan δ 0)	0.390	0.376	0.346
Rolling Resistance (tan δ 60)	0.137	0.162	0.16

rotors. A 2-roll mill was used to sheet out batches in between mixing stages. A U-Can Dynatex Mooney viscometer was used to measure Mooney viscosity ML(1+4) values. A U-Can Dynatex moving die rheometer was used to measure cure properties including Ts1 scorch and T90. Viscoelastic properties were measured on a Netzsch Gabometer dynamic mechanical analyzer with tangent delta @0°C values used to predict wet traction and tangent delta @60°C values used to predict rolling resistence. A Jeol JCM NeoScope benchtop scanning electron microscope (SEM) was used to measure silica dispersion obtained at 100x magnification. NIH ImageJ software[19] was used to analyze SEM data and give quantitative results on percent-white areas and average particle size distributions.

OSC is ISO 9001, ISO 14001 and OHSAS 18001 certified by Bureau Veritas, has Ecovadis 2022 Silver Sustainability Rating, and is REACH Compliant.

Fig. 10: Graph of %-white areas from imageJ analysis of SEM@100X for three levels of zinc process additive in a model tire tread.

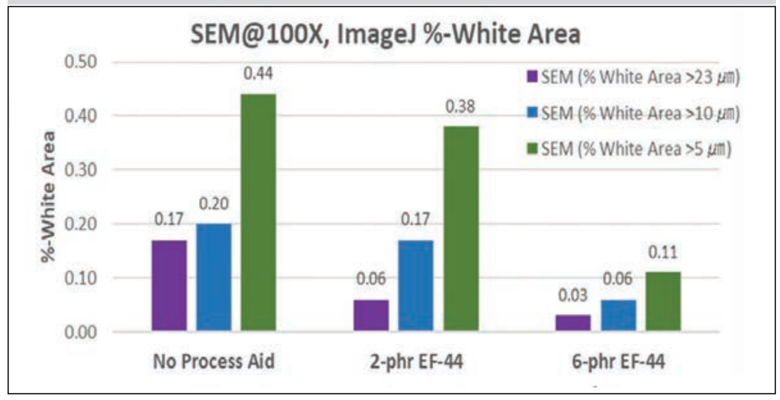
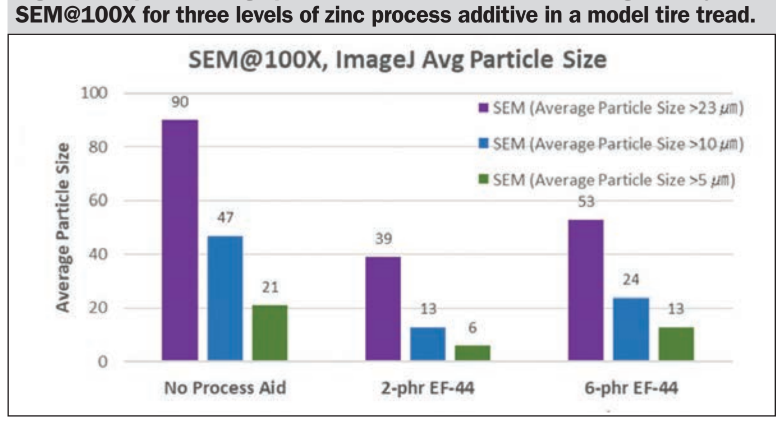


Fig. 11: Graph of average particle size distributions from imageJ analysis of SEM@100X for three levels of zinc process additive in a model tire tread.



Results and discussion

High-load, high-surface area silica tread

Formulations of high loadings of high surface area silica (BET ~210 m^2/g) in model PCR tire treads were identified from literature.[20-23] A formulation was selected to initiate OSC exploratory investigations on how to: (1) best incorporate and disperse 100-phr of a high-surface area silica, (2) establish the best addition and mixing sequence of all ingredients so as to disperse silica and minimize the percent-white area from SEM data, (3) promote the surface hydrophobation reaction of silica with the bifunctional organosilane[3,24],

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(4) adjust the levels of the organosilane, processing additives and curatives to optimize the M300/M100 reinforcement index value, and (5) directly compare the sustainable Nzerosil RH-230G made from renewable rice husk to three commercial high surface area silicas. Due to the high number of primary and interacting variables needed to be examined, it was not feasible to use statistically design experiments, but to use tread compounding information and experiences.

The highly dispersible, high surface area Eecosil 230MG microgranular silica[18] was used for exploratory mixes in a 75/25 SSBR/high-cis BR tread compound. Our prior results were that silica addition needed to be split into three steps, with a maximum of 80-phr being incorporated into the first mixing stage. A 55/25-phr silica split in the first pass gave good dispersion to minimize the %-white area and reduce the average particle size distributions based on ImageJ analysis of SEM data obtained at 100x magnification. We also previously determined to add all of the organosilane coupling agent with the first 55-phr silica addition. The 25-phr silica, carbon black and processing oil was added together later during the first stage of mixing. The remaining 20-phr silica was added in the second mixing step along with more processing oil to help incorporate it quickly. A 4-pass mixing sequence was the starting procedure **Table 1**.

Table 5: Key process, physical and viscoelastic test results of high surface area silica treads.

Property	NZEROSIL™ RH-230G	Eecosil 230MG	Eecosil 230G	Silica 1
Mooney Viscosity (ML(1+4)@100°C)	89.9	93.6	98.1	82.6
Ts1 (min)	5.7	4.2	4.9	5.7
T90 (min)	13.9	13.6	14.0	14.1
Tensile (MPa)	8.6	7.4	8.3	5.9
Elongation at Break (%)	376.3	334.4	344.3	301.0
100% Modulus (MPa)	1.9	2.1	2.5	1.8
300% Modulus (MPa)	6.4	6.5	7.1	6.1
Reinforcement Index (M300/M100)	3.31	3.04	2.84	3.29
Wet Traction (tan δ 0)	0.340	0.346	0.343	0.338
Rolling Resistance (tan δ 60)	0.154	0.160	0.165	0.172

Fig. 12: Bar graph of key tread properties of Nzerosil RH-230G relative to Eecosil 230MG (=100).

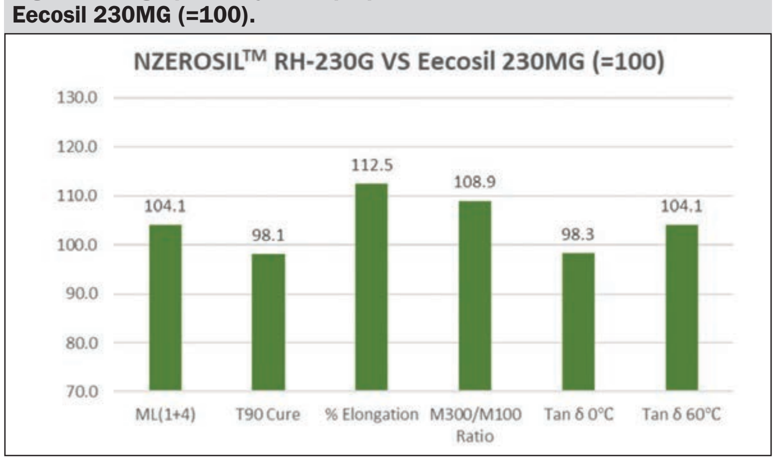


Fig. 13: Bar graph of key tread properties of Nzerosil RH-230G relative to Eecosil 230G (=100).

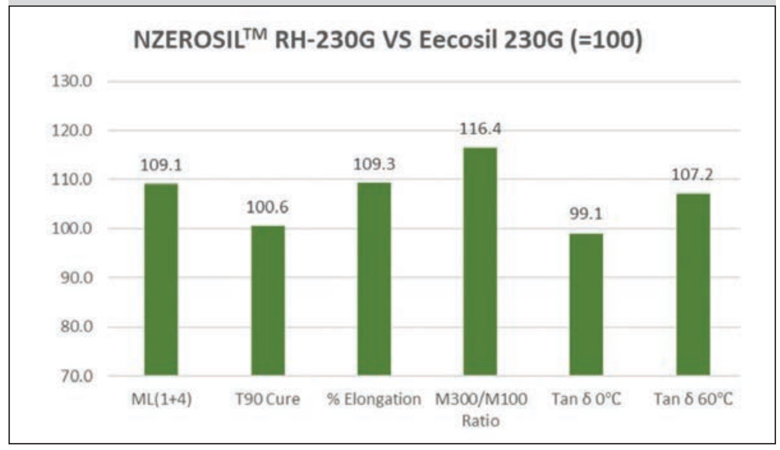
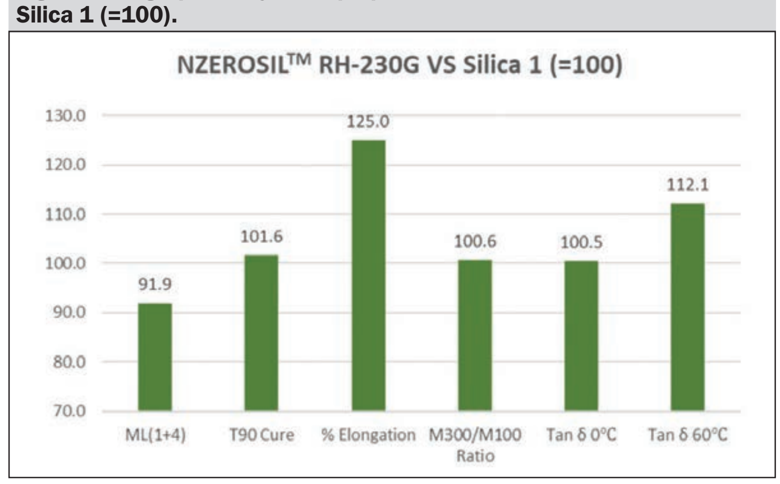


Fig. 14: Bar graph of key tread properties of Nzerosil RH-230G relative to Silica 1 (=100).



Mix sequence optimization

Ingredients in **Table 1** were mixed as shown in the 4-pass sequence using a 55-phr/25-phr silica split in the first stage. Two 5-pass mixes were made by adding a simple remill step after either the second pass 20-phr silica addition (Stage 3 remill), or after the remaining chemicals were added in the third pass (Stage 4 remill). A 6-pass mix was also evaluated by adding two remill steps, one each after the second-pass 20-phr silica addition step (Stage 3 remill) and again after adding the chemicals (Stage 5 remill). **Fig. 7** is a summary.

Cure and viscoelastic property results were comparable (**Table 2**). Both 5-pass mixes and the 6-pass mix sequences gave desirably lower Mooney viscosity values. Tensile testing showed that no compound had the desired elongation target of >300 percent, thus M300/M100 ratios could not be determined.

The percent-white areas from ImageJ analysis[19] of SEM @100X data (**Fig. 8**) showed that both the two 5-pass and the 6-pass mixes gave lower values compared to the 4-pass mixing sequence. The smaller average particle size distributions for the tread mixed in 5-passes with a Stage 3 remill (**Fig. 9**) was used to select this mixing sequence for follow-up studies.

Formula adjustments

Adding a processing additive, along with changes to coupling agent and/or curatives levels was studied to increase the elongation to >300 percent in order to obtain M300/M100 reinforcement index values. Tread compounds A, B and C were studied with 0-phr, 2-phr and 6-phr of Struktol EF-44 modified zinc soap.[25-26] CBS accelerator was reduced from 2.4-phr to 1.5-phr in compounds B and C, and the organosilane coupling agent was reduced from 10-phr to 8-phr in compound C containing the 6-phr of zinc additive (**Table 3**).

Use of the zinc processing additive changed several properties.[25-26] Elongation at 300 percent was highest for compound C using 6-phr zinc additive. Mooney viscosity values were desirably decreased, but T90 cure times were increased, and predicted wet traction and rolling resistance (tangent delta @60°C increased) values were undesirably reduced (**Table 4**).

Percent-white area values decreased using the zinc processing additive, with compound C (6-phr additive) giving the lowest values (**Fig. 10**). However, the average particle size distributions were lowest for compound B using 2-phr of the zinc dispersant (**Fig. 11**). Thus, the optimum level of zinc soap would need to be determined based on the specifics of the formulation.

Sustainable Nzerosil RH-230G

Tread compound C with 6-phr of zinc processing additive (**Table 3**) was used to evaluate the performance of high surface area (BET ~210 m^2/g) silicas at 100-phr to model an ultrahigh performance passenger, EV or light truck tire tread. Sustainable Nzerosil RH-230G granulated silica and three commercial high surface area silicas were studied: Eecosil 230MG microgranular, Eecosil 230G granulated, and microgranular Silica 1. All four 100-phr silica-filled model treads were mixed using the 5-pass sequence with Stage 3 remill (**Fig. 7**).

Testing showed that Nzerosil RH-230G has comparable performance to the Eecosil 230MG and Eecosil 230G silicas since most values are within 10 percent of one another (**Table 5, and Figs. 12 and 13**). Mooney viscosity is lowest, and Ts1 scorch, tensile strength, elongation at break, and M300/M100 reinforcement index values are the highest. Nzerosil RH-230G has a higher tensile strength and elongation at break, and lower predicted rolling resistance compared to Silica 1 (**Fig. 14**).

SEM@100X / ImageJ analysis dispersion showed that the highly dispersible Eecosil 230MG microgranular silica gave significantly lower percent-white area values. Nzerosil RH-230G had comparable values to Silica 1 (**Fig. 15**). No notable differences were observed for average particle size distributions (**Fig. 16**).

In a 100-phr silica-filled tire tread modeled for ultrahigh performance and EV passenger car, and for light truck tire treads, sustainable high surface area Nzerosil 230G granular silica made from bio-renewable rice husk gave equivalent performance to granulated Eecosil 230G and microgranular Eecosil 230MG silicas made from glass cullet. Performance is slightly better versus competitor Silica 1. A 5-pass mixing sequence with a simple remill step is required to disperse silica in order to reduce the percent-white area values.

Fig. 15: Graph of %-white areas from SEM@100X/ImageJ analysis of Nzerosil RH-230G, Eecosil 230MG, Eecosil 230G and Silica 1 treads.

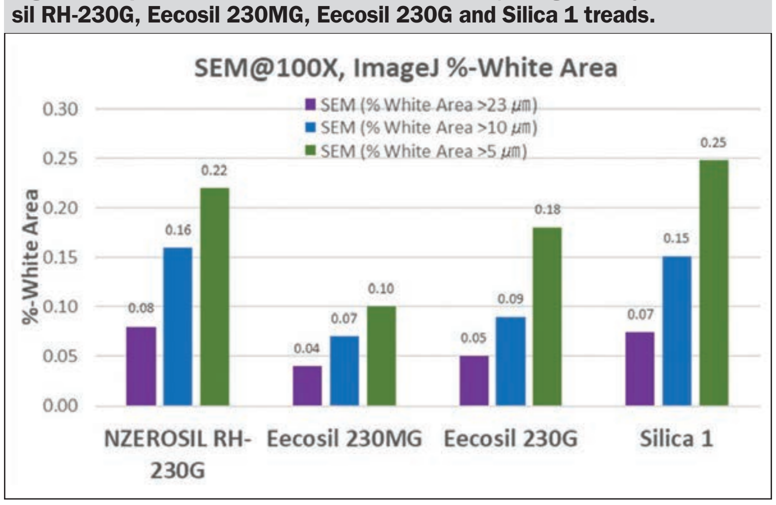
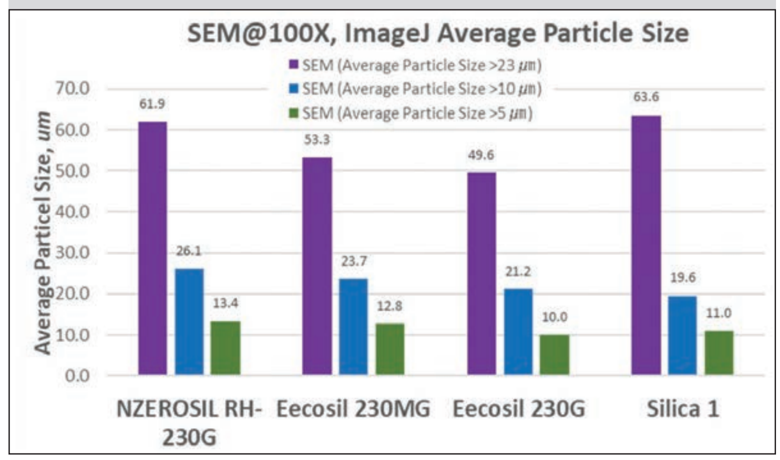


Fig. 16: Graph of average particle size distributions from SEM@100X/ imageJ analysis for Nzerosil RH-230G, Eecosil 230MG, Eecosil 230G and Silica 1 treads.



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