Improving SSBR performance for hybrid and electric vehicles

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Matching sustainability with tire performance will be the new challenge that both polymer producers and tire makers will have to face jointly.

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Executive summary

Electric vehicles and low-emission hybrid cars are driving the transformation of mobility. This means it's time to learn more about new materials, which can help target the rolling of high-tech tires into carbon neutrality and ultimately into a CO2 emission-free future.

An investigation is then presented for providing tire tread compounds for hybrid and electric vehicles, containing specially designed SSBR and BR grades. Targeted key properties for the compounds are low hysteresis (lower rolling resistance) together with high grip and improved abrasion resistance.

The compound sustainability comes from the use of bio-attributed styrene and butadiene monomers through bio-naphtha, mass balance approach and ISCC-plus certification.

In fact, electric engine torque has a positive and negative side. On the one hand, it means instant acceleration. On the other hand, this high instant torque places additional strain on the tires. With instant torque, increased weight and lower emissions comes an even greater need for minimal rolling resistance.

To face such a demanding requirement, next-generation fn-SSBR for a stronger filler-polymer interaction is designed. Moreover, high-cis BR with optimized architecture also is taken into account in order to improve the compound's overall performance.

Sustainability further can be addressed through a circular economy approach, offering the integration of bio, bio-circular and circular feedstock as a replacement for fossil feedstock at refinery stage. The variable content of bio, bio-circular and circular feedstock in the final product is attributed through the Mass Balance approach to styrene and butadiene monomers.

ISCC-Plus certification is then applied. ISCC-Plus-certified polymers can be purchased with identical performance, quality and properties of traditional products. There is no need for new tests, new product development, technology adaptation, registration and regulatory approvals.

Table 1: Main typical properties of the raw polymers. All grades shown in the table are dry grades.

Versalis Europrene	Mooney mu	Sty %	Vin %	Cis %	Tg (DSC) °C	note
SOL R 72616	68	21	63	-	-25	Commercial fn-SSBR grade
New fn-SSBR *	61	27	59	-	-23	New generation fn-SSBR
Neocis BR	44	-	1	97	-107	Commercial Nd-BR grades
New Nd-BR (HP) *	44	-	1	97	-109	New polymer design

Table 2: Silica tread compound, which is rich in SSBR content. Other chemicals, typical of tire tread compounds, comprise antiozonant, antioxidants and suitable processing aid. Curing agents are ZnO, stearic acid, DPG and sulfenamide-based accelerator in amounts typical of tire practice for conventional curing. This experiment aims at investigating the effect of SSBR types, using different generations of functional groups.

Silica tread #1	phr
Fn-SSBR (dry)	85
Neocis BR	15
Silica	86
Silane	6.6
CB	7
Process oil	16
sulfur	1.3

Experimental

Styrene-butadiene copolymers and polybutadienes are Europrene grades by Versalis. The main properties of the used raw polymers are summarized in **Table 1**.

More precisely, a new development for SSBR is proposed. With respect to the commercially available grade SOL R 72616, this new development—herein referred to as "New fn-SSBR"—has slightly different sty/vin composition and Mooney viscosity (also slightly different molecular architecture). But it especially features a new-generation functional group, which is specifically introduced to boost chemical interaction between polymer matrix and filler particles in the compound phase.

As for high-cis-BR based on neodymium catalyst, together with commercially available Neocis grades by Versalis, we also introduce in this investigation a new BR development, referred to as "New Nd-BR (HP)" in the presentation. The latter is specifically designed for high performance compounds.

Compounding was carried out using laboratory internal mixers with Banbury-brand rotors. Physical and mechanical properties of rubber compounds were measured according to ASTM, DIN or ISO standards. The Rolling Resistance Index on vulcanized specimens was determined through strain sweep measurements using a torsional bar (5-percent strain, 10 Hz, 60°C). An RPA is used to check results on different specimen geometry at higher deformation level. Temperature sweep tests on vulcanized specimens were carried out with torsional bar geometry at 0.1-percent strain, 1 Hz and 2°C/min.

Results and discussion

Compound results are shown in the following narrative, where the experimental tests are listed in separated sections to improve the readability of results. All the tests refer to silica tread compounds, but recipes with different polymeric blend ratios and filler loadings were considered.

Silica tread No. 1: Effect of fn-SSBR

In the first experiment, we mixed polymers according to the recipe shown in **Table 2**, which is rich in fn-SSBR (85 phr). Test results are available in **Fig. 1.** All the major properties improve upon replacing SOL R 72616 with the new fn-SSBR grade, with RR and WG predictors significantly improved.

In **Fig. 2** we plot the result of DMA tests (loss tangent) carried out on cured torsional bars at different temperature values. The plot clearly shows the impact due to the new fn-SSBR polymer

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Fig. 1: Compound test results refer to the recipe shown in Table 2. Data was indexed according to the performance criterion. The compound based on SOL R 72616 is the reference case (solid line), so each property is indexed to 100. The result of the compound based on the new fn-SSBR grade are shown in comparison (dashed line). Independently of the specific property, indexed results with digits ≥ 100 indicate improved performances. The wet grip predictor is not fitting inside the radar plot due to tremendous improvement achieved for the compound based on the new fn-SSBR polymer (the WG predictor index approaches +50% improvement).

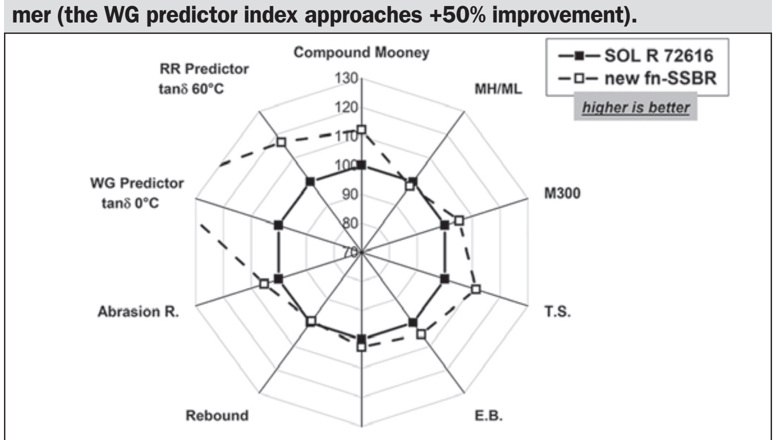


Fig. 2: Temperature sweep results of compounds referring to the recipe shown in Table 2. Measurements are carried out in torsion at low deformation level (0.1% strain). When using the new fn-SSBR polymer, the loss tangent peak gets significantly impacted in the [-20; +20°C] temperature range.

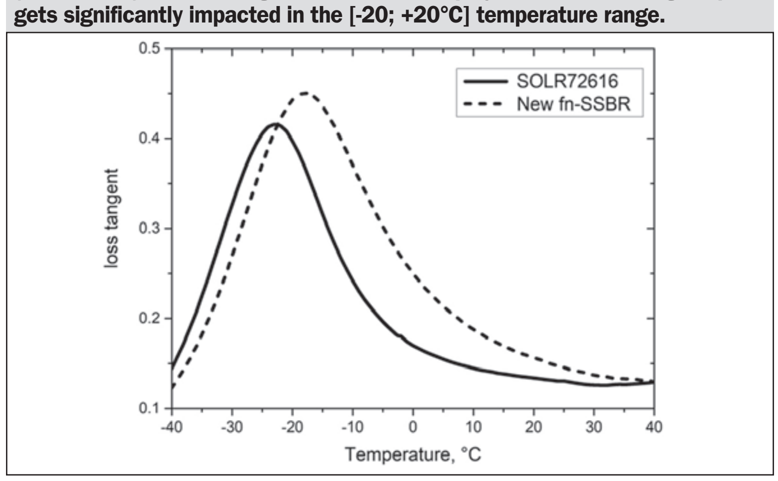
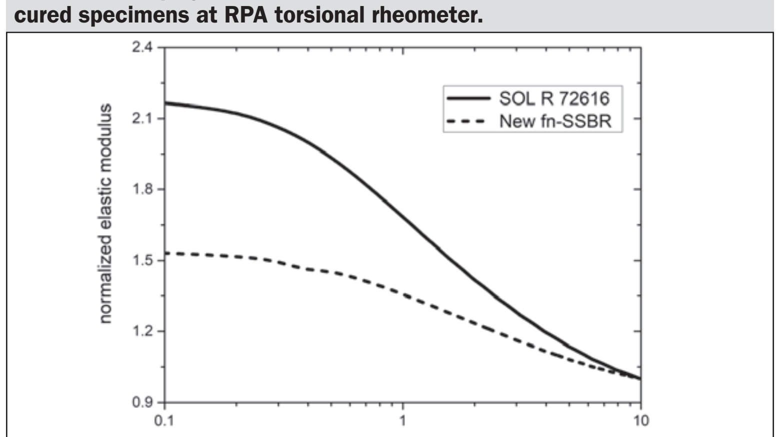


Fig. 3: Strain sweep results of compounds referring to the recipe shown in Table 2. Measurements are carried out in torsion at 10 Hz and 60°C. Depending on the used fn-SSBR type, different elastic properties are observed. Reduced Payne Effect is found for the compound based on the new fn-SSBR polymer. Such results also are confirmed on tests on uncured specimens at RPA torsional rheometer.



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(dashed line). More precisely, its peak gets higher, broader and located at higher temperature values. This shift not only is due to the different polymer Tg between SOLR72616 (-25°C) and the new fn-SSBR grade (-23°C), as the shift of loss tangent peak is greater for the compound.

The observed difference in the peak region is affected by two major aspects for the new fn-SSBR polymer: the use of a new generation functional group and a different molecular weight distribution. The new functional group determines more efficient chemical interaction between the rubber matrix and the filler particles, thus significantly limiting the filler flocculation process.

In addition, we expect that the different elasticity of the new fn-SSBR grade has contributed to provide a more efficient filler dispersion into the rubber matrix. It is known in the literature[1] that SSBR polymers with different macromolecular structures and functional groups do affect the degree of filler dispersion inside the rubber matrix. Also with regards to this topic, it has been published that there is a more general effect of molecular weight on carbon black dispersion in NR/SBR and BR/SBR blends.[2]

Our findings in temperature sweep and strain sweep test results also are in line with the literature,[3] where the authors show that, for a given compound (silica compound based on SBR polymer), when filler-filler shielding agent or polymer-filler coupling agent are introduced, the location and the height of the loss tangent peak are significantly impacted with respect to the untreated compound. Meanwhile, the authors also show that the introduction of the above-mentioned ingredients leave substantially unaffected the loss modulus peak, thus not altering the glass transition temperature of the polymer.

As a consequence of this more efficient interaction between polymer and filler particles together with a limited filler flocculation process, the Payne Effect is significantly reduced for the new fn-SSBR, as we show in **Fig. 3**. This result is again in line with literature data.[4]

Silica tread No. 2: Effect of high-cis BR

In the second experiment, we mixed polymers according to the recipe shown in **Table 3**, which always applies the same SSBR polymer, while the Nd-BR type is changed. With respect to the formulation shown in **Table 2**, this silica tread recipe is richer in Nd-BR content in order to emphasize its effect on compound properties.

In **Table 4**, the major compound properties are summarized, showing that the compound properties significantly improve when replacing Neocis BR with the more advanced Nd-BR types, i.e. the new Nd-BR (HP), respectively. This improvement of properties is not limited to conventional tire traction predictors (i.e., RR and WG), but also embraces the mechanical properties. In particular, tensile properties and abrasion resistance are sensibly boosted. Those both are popularly acknowledged as rough predictors of tread durability and its resistance to wear.

Figs. 4 and 5 show the impact of the Nd-BR types on the loss tangent curve and the Payne Effect, respectively. Depending on the specific formulation as well as on mixing equipment and the related mixing conditions, the effect of Nd-BR can become relevant, as it can allow the rubber matrix to achieve an appropriate level of elasticity during the compounding step.

Consequently, the filler dispersion becomes efficient[5] and the final requirements can be ultimately matched on vulcanizates. It is, thus, extremely important that the most appropriate combination of SSBR and Nd-BR types is accounted when willing to target the final properties of a high-performance tire tread compound.

Insight into unfilled compound

In this section, we provide an insight into DMA tests (temperature sweeps) of unfilled cured compounds based on the polymeric blend ratio SSBR/BR=85/15. The used recipe is the one referring to **Table 2**, which had been modified by removing both silica and silane from the ingredients. Unfilled compounds then were mixed and finally cured to run DMA tests on vulcanizates in torsion.

In **Fig. 6** we show the plot of compounds using the same Neocis BR material but different fn-SSBR type. More precisely, in the compounds, SOL R 72616 is compared with the new fn-SSBR grade.

In **Fig. 7**, not only the SSBR type, but also the Nd-BR grade is replaced. Due to that, the compound based on commercially available products can be directly compared with the one based on the newly developed materials, those being the new fn-SSBR and the new Nd-BR (HP).

As expected, in both plots there is no evidence of significant impact due to the replacement of one single material (SSBR) or replacement of both grades at the same time. Moreover, **Fig. 7** focuses on the range temperature where the loss tangent peaks are located.

We notice a slight shift in the position of the local maxima, but the entity of this shift is compatible with the glass transition temperature (Tg) values of the raw polymers (**Table 1**). Also, no remarkable effects are observed on the investigated SSBR/BR unfilled systems due to the different elastic properties (or molecular weight differences) of the newly developed polymers with respect to the commercial SSBR/BR products.

Due to that, we get a further confirmation that the different results found for the filled compounds (as previously observed and commented in the sections Silica tread No. 1 and Silica tread No. 2) are explained by different levels of filler dispersion; that each SSBR/BR combination allows achieving during the mixing phase, together with the effect of the new-generation functional group of the new fn-SSBR polymer. This latter acts in particular on top of the improved filler dispersion, as it also greatly limits the filler flocculation.

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Table 3: Silica tread compound, which is richer in BR content with respect to the formulation shown in Table 2. Other chemicals comprise antiozonant and antioxidants. Curing agents are ZnO, stearic acid, DPG and sulfenamide-based accelerator in amounts typical of tire practice for conventional curing. This experiment aims at investigating the effect of BR types on the compound properties.

Silica tread #2	phr
Fn-SSBR (dry)	67
High-cis-BR (Nd)	33
Silica	95
Silane	7.6
CB	4
Process oil	27
Hydrocarbon resin	7.5
Sulfur	1.6

Table 4: Compound test results refer to the recipe shown in Table 3. Data were indexed according to the performance criterion. All the compounds use the same SSBR polymer, while Nd-BR can be different. The compound based on Neocis BR is the reference case, so each property is indexed to 100. When using the new Nd-BR (HP) grade the results of the compounds are indexed in comparison with the reference case. Independently of the specific property, indexed results showing digits ≥ 100 indicate improved performances (higher is better).

	Neocis BR	New Nd-BR (HP)
M300	100	105
Tensile Strength	100	107
Elongation at Break	100	101
Hardness	100	105
Rebound @ RT	100	109
Abrasion Resistance	100	113
HBU	100	99
WG predictor (tanδ @0°C, 0.1%)	100	113
RR predictor (tanδ @60°C, 5%)	100	113
RR Predictor (tanδ @ 60°C, RPA)	100	108

Fig. 4 Temperature sweep results of compounds referring to the recipe shown in Table 3. Measurements are carried out in torsion at low deformation level (0.1% strain). When using the new Nd-BR (HP) polymer, the loss tangent peak gets significantly impacted in the whole peak region. Due to that, the wet grip predictor gets significantly affected (loss tangent @ 0°C is higher). Although the applied deformation level is low during this test, at high temperature values lower energy dissipation is found for the new Nd-BR (HP), with that being beneficial for rolling resistance. Such a result was confirmed by dedicated DMA tests carried out at higher strain level (see Table 4).

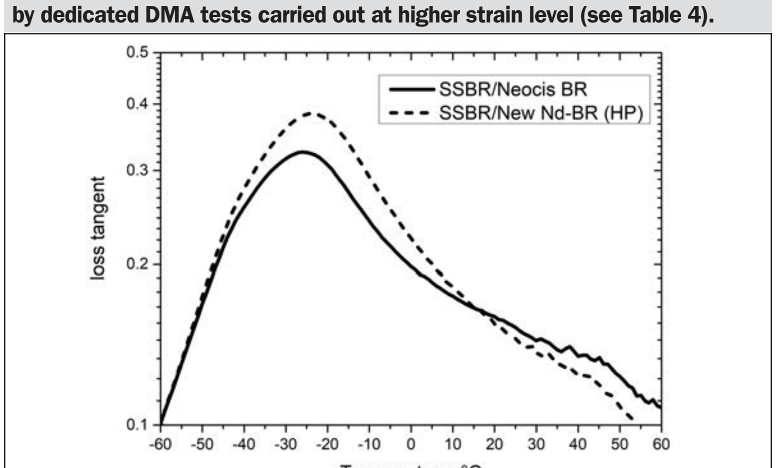


Fig. 5 Strain sweep results of compounds referring to the recipe shown in Table 3. Measurements are carried out in torsion at 10 Hz and 60°C. Depending on the used Nd-BR type, different elastic properties are observed. Reduced Payne Effect is found for the compound based on the new Nd-BR (HP) polymer. Such results are confirmed also by tests at RPA torsional rheometer on cured specimens at higher deformation level.

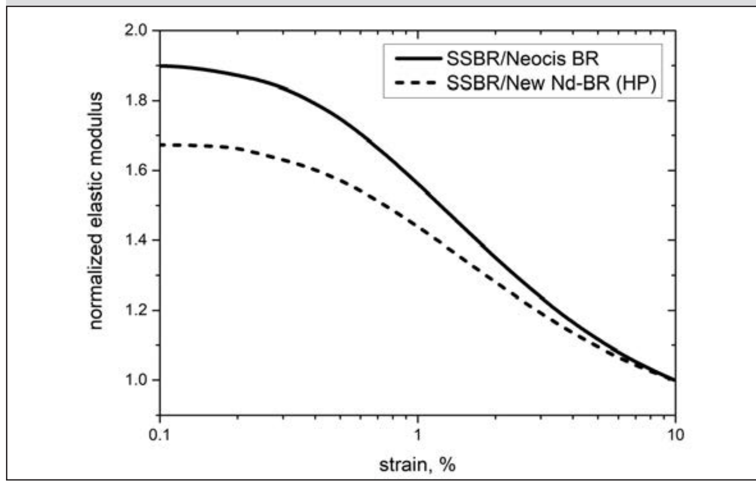


Fig. 6: Temperature sweep test results for unfilled compounds using an SSBR/BR=85/15 polymer ratio. Results are in line to expectations, as no significant difference are observed in the curves when applying a 1:1 replacement of the fn-SSBR type (the same commercial Neocis BR type by Versalis is used for both compounds).

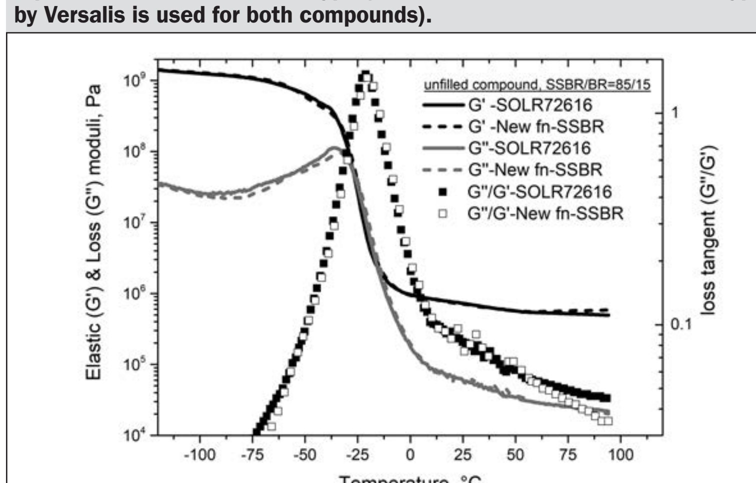
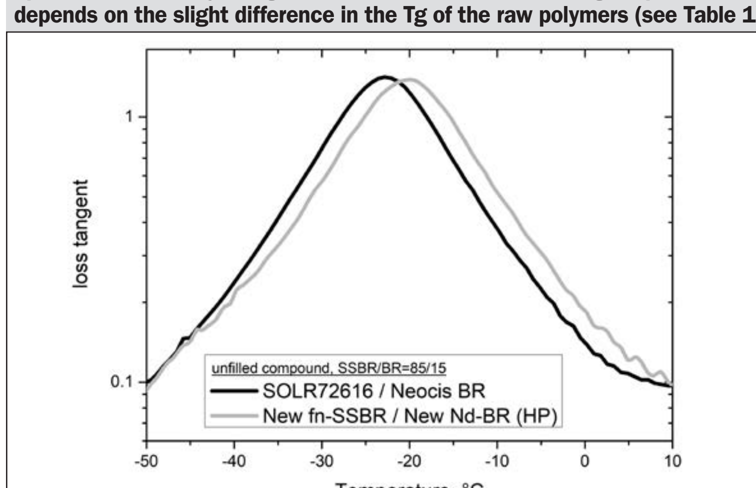


Fig. 7: Temperature sweep test results (loss tangent curves) for unfilled compounds using an SSBR/BR=85/15 polymer ratio. Results are in line to expectations, as no significant difference are observed in the curves when 1:1 replacing the commercially available SSBR/BR grades with the newly developed materials. Only a slight shift is found for the loss tangent peak, which depends on the slight difference in the Tg of the raw polymers (see Table 1)



Cabot expands E2C offerings for durability, sustainability

By Patricia Faulhaber
Rubber News Correspondent

BOSTON—Cabot Corp. recently committed to becoming a change agent and set a goal to have net-zero emissions by 2050.

To help reach that goal, Cabot has expanded its Engineered Elastomer Composites (E2C) product line with the introduction of two new solutions, the E2C FX9570 and E2C EX9620 products.

Both are intended to provide rubber manufacturers with additional options to design products for high durability in demanding operating environments. In addition, the newest composites will help deliver improvements in durability and heat minimization that have benefits in off-the-road tires like aircraft and port tires, truck tires used on rough surfaces, as well as in other industrial rubber products exposed to severe wear conditions or high operating temperatures.

"Our Engineered Elastomer Composites (E2C) product line is a core element of our sustainability strategy for the tire and rubber industry and plays an essential role in enabling a lower carbon future," said David Reynolds, vice president and general manager of Cabot Engineered Elastomer Composites. "By enabling long-lasting and energy-efficient rubber products, we are making the most efficient use of raw materials, reducing downstream greenhouse gas emissions and reducing the number of end-of-life tires. In addition, by delivering premixed composites to our customers, we are helping them reduce the energy requirements in their own operations."

Reynolds added that in 2020, Cabot launched its first set of E2C products targeted primarily at earthmover tire applications. Customers quickly found additional uses for the E2C line.

"As customers began working with these products, they quickly realized how our E2C platform can deliver truly unique and differentiated rubber properties, and formulated our products into a wider range of rubber products. Through that process, we ultimately identified a new set of performance challenges faced by our customers, and developed these products to offer a different performance signature," said Reynolds.

Cabot has committed to net-zero emissions by 2050.

The company's E2C solutions offer three performance series—Durability, Efficiency and Foundation.

"Solutions in the Durability series are designed to reduce in-field failures, extend tire/compound life environments and maximize operational uptime," Reynolds said. "The solutions in our Efficiency series are designed for cool-running rubber compounds without other performance compromises. Furthermore, solutions in our Foundation series are designed to deliver multidimensional performance in a variety of applications."

Starting with Durability, Cabot's E2C FX9570 and E2C EX9620 solutions provide rubber manufacturers with additional options to design products for high durability in demanding operating environments.

The E2C EX9620 product is the first solution released in Cabot's Efficiency series and is designed to enable cool-running rubber compounds with strong resistance to abrasion and cutting. EX9620 is optimally deployed in applications where rubber products are subject to excessive heat loads caused by high operating speeds, heavy loads, long-duty cycles and/or high temperatures.

The E2C FX9570 product is part of the company's Foundation series and enables high rubber durability in rough environments where cutting and chipping is prevalent, and duty cycles demand higher heat resistance. FX9570 lowers heat build-up by up to 20 percent versus conventional compounds, the company said.

The customer response to the latest E2C solutions has spurred ideas for possible additional uses. The basic process of making rubber compounds has been around for many years and today, rubber compounders must work incredibly hard to squeeze additional performance from these conventional processes.

"When customers test our E2C products, they consistently tell us that the degree of performance improvement enabled by E2C is unmatched and that they want to apply the technology to a wider range of technical problems and applications," Reynolds said.

Cabot's E2C solutions enable rubber product manufacturers to simplify the commercialization of differentiated products through the availability of high-performance, pre-mixed composites delivered in an easy-to-handle product form. Enabled by proprietary process technology that mixes reinforcing agents into elastomers, E2C solutions can be integrated into the current production methods of rubber compounders without additional investment, enabling faster product development and more flexible innovation.

By improving product performance, E2C solutions also deliver economic and sustainability benefits for rubber product manufacturers and their customers, as Cabot said products made with E2C solutions have been demonstrated to last 15-30 percent longer than products made with conventional compounds and enable a more fuel-efficient operation by reducing energy loss in rubber components.

Cabot offers the E2C pre-mixed rubber compound.

Additional types of products that can benefit from using the E2C FX9570 and EX9620 lines include those exposed to high operating temperatures, such as aircraft, port and earthmover tire treads; on-road truck tire treads used on mixed surfaces or in places where road infrastructure is underdeveloped and where the requirements include both durability and low rolling resistance; and industrial rubber product applications where energy efficiency and severe wear resistance are critical, such as in mining applications like slurry pump, hydro-cyclone and mill liners, screen panels and conveyor belt top covers.

"Our E2C product line is targeted at enabling sustainability across the rubber industry and durability is only one dimension," Reynolds said. "Our current products can also enable significant reduction in tire rolling resistance, improving vehicle fuel economy, and reducing greenhouse gas emissions. Future products will be focused on enabling these benefits in an even wider range of tire and industrial rubber products."

Cabot's E2C solutions family also includes the E2C DZ8650, E2C DX9730, E2C DX9640 and E2CFX9390 products. Recently, Cabot's E2C product line was named to *European Rubber Journal*'s "Top 10 Elastomers for Sustainability" list for the second time. This list ranks the most important development projects focused on enhancing the sustainability of elastomers and rubber materials.

Cabot Corp. is a global specialty chemicals and performance materials company headquartered in Boston. The company is a leading provider of rubber and specialty carbons, engineered elastomer composites, inkjet colorants, masterbatches and conductive compounds, fumed silica and aerogel.

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Silica tread No. 3: Formulation for hybrid/EV tires

Table 5 shows the details of the proposed recipe for EV tire tread. Natural rubber is introduced in the SBR/BR blend to provide beneficial effect on the mechanical performances. Compound results are summarized in **Table 6**, all indexed according to the performance criterion, where the reference compound uses SSBR/BR commercial grades by Versalis. The reference compound is thus compared with the compound obtained by mixing the newly developed polymers, new fn-SSBR and new Nd-BR (HP). Despite the introduction of NR as the third polymer in partial replacement of SSBR, the combination of the newly developed SSBR/BR polymers still obtains significant enhancement of the cured compound properties with respect to the reference case.

In particular, the following properties are improved: tensile modulus at 300-percent elongation, abrasion resistance, rebound, and RR and WG (DMA predictors), which are all major properties of interest to the tire treads for EV vehicles. It is, in fact, largely debated that such new tire treads do and will require higher durability as well as sensible reduction in the tire energy losses.

Finally, we observe a slightly lower compound Mooney for the compound based on the newly developed SSBR/BR grades. This is an interesting achievement, which needs to be further investigated, as a lower compound viscosity is expected to provide improved processability behavior to the uncured compound. Further tests are currently ongoing at laboratory scale to explore this behavior and consolidate the result.

Table 5: Silica tread compound for EV tires. The ingredient amounts are in phr. The other chemicals comprise antiozonant, antioxidants, compatibilizer for polymers and processing aid. Curing agents are ZnO, stearic acid, DPG and sulfenamide-based accelerator in amounts typical of tire practice for conventional curing.

Silica tread #3	SOL R 72616 / Neocis BR	New fn-SSBR / New Nd-BR (HP)
Fn-SSBR (dry)	55	55
NR (CV60)	15	15
High-cis-BR (Nd)	30	30
Silica	100	100
Silane	8.0	8.0
CB	5	5
Process oil	24	24
Hydrocarbon resin	4	4
Sulfur	1.0	1.0

Table 6: Compound test results refer to the recipe shown in Table 5. Data was indexed according to the performance criterion. The compound based on commercial grades is the reference case, so each property is indexed to 100. When using the newly developed materials, compound results are indexed in comparison with the reference case. Independently of the specific property, indexed results ≥ 100 indicate improved performance. That is the case for the compound based on the newly developed grades (higher is better).

	SOL R 72616 / Neocis BR	New fn-SSBR / New Nd-BR (HP)
MS (1+4) @100°C (Master), mu	100	106
MS (1+4) @100°C (Final), mu	100	107
M300, MPa	100	115
TS, MPa	100	101
Hardness, Sh.A	100	101
Rebound, %	100	111
DIN Abrasion, mm3	100	118
WG predictor (tanδ @0°C, 0.1%)	100	118
RR predictor (tanδ @60°C, 5%)	100	112

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