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Tire road wear particles
Natural rubber biosynthesis
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Simulating tire wear

2023 Annual Review

The Annual Review of Tire Materials and Tire Manufacturing Technology

CONTENTS

4 **Foreword**
by Matt Ross, editor-in-chief, *Tire Technology International*

SECTION 1: DESIGN, MATERIALS, TESTING AND FUTURE POSSIBILITIES

8 **Evaluating TRWP**
Frank Schmerwitz, Continental, Germany
Employing tire tread markers in the evaluation of tire wear behavior under real-world testing conditions

12 **Tire wear particle toxicity**
Dr Zhengchu Tan, Dr Alex Berry, Prof. Maria Charalambides, Dr Ana Mijic, Dr Will Pearse, Prof. Alexandra Porter, Prof. Mary P Ryan, Prof. Robert N Shorten, Dr Marc E J Stettler, Prof. Terry D Tetley, Dr Stephanie Wright and Dr Marc A Masen, Imperial College London, UK
Exploring the origins, composition and behavior of tire wear particles, and considering the possible effects on humans and the environment

16 **Evaluating wear testing**
Xiao-Dong Pan, Xingwang Dong, Zhengying Li and Jiahuan Li, Zhongce Rubber Group, China
An investigation into the behavior of the conventional Lambourn wear tester, examining the consequence of inconstant slip control

24 **Assessing tire wear**
R Stoček, PRL Polymer Research Lab, Czech Republic and Centre of Polymer Systems, Tomas Bata University, Czech Republic; G Heinrich, Technische Universität Dresden, Institut für Textilmaschinen und Textile Hochleistungswerkstofftechnik, Germany; and R Kipscholl, Coesfeld, Germany
The importance of accurate data concerning tire tread wear performance has led to development of a range of sophisticated testing equipment

28 **Simulating tire-wear physics**
Giovanni Narducci, MegaRide; Flavio Farroni and Aleksandr Sakhnevych, University of Naples Federico II, Italy
A new module for a tire simulation platform estimates the evolution of tread thickness by calculating the contribution of abrasion and performance degradation

32 **Tire-road friction testing**
Agate Utane and Dr Georgios Mavros, Loughborough University, UK
Developing a new test rig to measure friction on the surface of a stationary tire, thus removing the need for mounting on a testing setup

36 **Repeatable dynamic testing**
Heidi Franklin, A&D Technology, USA
Sophisticated use of testing methods and data gathering are integral to gathering dynamic tire footprint measurements in an accurate – and repeatable – manner

40 **Impact of silica on tire tread**
Zuzanna Andrzejewska,[1,2] Wisut Kaewsakul,[2] Raymond Zeeman,[1] Louis A E M Reuvekamp[1,2] and Anke Blume[2]
[1] Apollo Tyres Global R&D, Netherlands
[2] University of Twente, Faculty of Engineering Technology, Department of Mechanics of Solids, Surfaces and Systems, Chair of Elastomer Technology and Engineering, Enschede, Netherlands
Examining the effect of different silica types, which have become increasingly used in tire production, on the resulting tread rubber

46 **Studying hydrogenated SBR**
Shuichi Karatsu, Toyo Tire Corporation, Japan
Elucidation of the high-strength mechanism of hydrogenated styrene-butadiene rubber using coarse-grained molecular dynamics simulation

50 **Sustainable process oils**
Raúl Romano, Repsol Lubricantes y Especialidades, Spain
Evaluating the effect of bio-origin oil on vulcanization and its impact on rubber and filler relationships when used in tire compounds

54 **Natural rubber biosynthesis**
Haruhiko Yamaguchi, Yukino Miyagi-Inoue, Kenichi Uesaka, Sumitomo Rubber Industries, Japan
Researching the mechanisms at the heart of natural rubber biosynthesis and the development of enzymes

58 **Testing processing promoters**
Dr Cristian Oprisoni and Dr Antonia Albers, Lanxess, Germany
Investigating specially designed, increasingly sustainably based processing promoters and their role in improving the performance of tire tread compounds

62 **Predicting tire noise levels**
Sung-Uk Hwang and Sung-Hyun Jeong, Nexen Tire, South Korea; Youngsam Yoon, Hyundai Motor Company, South Korea; and Sang-Kwon Lee, Inha University, South Korea
A collaborative research project has explored the application of artificial intelligence and big data analysis to designing tires with lower levels of road noise

64 **Fleet debris study**
Nikhil Antony Joseph, Bridgestone EMIA. Contributors: Gary Powell and Peter Moulding, Bridgestone EMIA
An analysis of various types of debris collected at fleet depots and their potential to cause penetrations or puncture-related damage to tires, leading to tire failure

72 **Bio-based oil in real tires**
C Silvestri, Nynas, Italy; K Alavi and P Salomonsson, Nynas, Sweden; and H Fruhmann, Nynas, Austria
A new study expands on previous work by examining the performance of bio-based tire oil in real-world ultra-high-performance summer tires

76 **Studying plasticizer migration**
Sankar Raman Vaikuntam, André Wehmeier and Jens Kiesewetter, Evonik Operations – Smart Materials, Applied Technology Tire & Rubber, Germany; and Sara Liébana Viñas, Evonik Operations – Smart Materials, Coating & Adhesive Resins, Germany
Exploring the use of silane functionalized liquid polybutadienes for enhanced rubber performance and low migration in natural rubber-silica/silane systems

SECTION 2: PRODUCTION, QUALITY AND RECYCLING

82 **GTR devulcanization review**
Rounak Ghosh, Anke Blume and Wilma Dierkes, University of Twente, Netherlands
A review of recent advances in the field of devulcanization of end-of-life tires, particularly for rubber types used in the tire industry

90 **Electric heating for tire curing**
Edvin Sun, Himile, China
A newly developed system for generating the heat used in the curing process offers a range of operational and sustainability benefits

94 **Digitalizing the tire industry**
Amirhossein Shahdadi, Barez Industrial Group, Iran
Examining why increased application of digitalization can be implemented for the benefit of tire manufacturing operations

102 **Retrieving aramids from ELTs**
Noor Hossain, Teijin Aramid, Netherlands
Development of physical and chemical recycling routes for tire-grade, recycled para-aramid yarn is underway, but will benefit from industry-wide collaboration

106 **Efficient tire production**
Dali Krstic, Black Donuts, Finland
Using efficient manufacturing processes, and monitoring production and utility consumption, can yield valuable insights when skillfully implementing an MES

110 **Multipurpose calendering**
Marco Putignano, Comerio Ercole, Italy
A new calendering layout configuration is designed to integrate rubber sheet and innerliner gum processes into fabric and steel cord rubberizing production

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Impact of silica on tire tread

Examining the effect of different silica types, which have become increasingly used in tire production, on the resulting tread rubber

by Zuzanna Andrzejewska,[1,2] Wisut Kaewsakul,[2] Raymond Zeeman,[1] Louis A E M Reuvekamp[1,2] and Anke Blume[2]

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In addition to the traditional reinforcing filler, carbon black, silica has increasingly been used in tire tread compounds. This is because silica can significantly reduce the rolling resistance of tires, improving fuel efficiency.[1] Because of the hydrophilic nature of silica, a silane coupling agent is added to the silica formulations to achieve adequate filler dispersion and strong chemical bonds between the silica and a hydrophobic or non-polar rubber.[2]

Due to the demand from tire producers for further improvements in compound performance – to meet OE tire requirements – silica manufacturers have developed a new type of silica, referred to as highly dispersible silica, with two key characteristics: specific surface area and structure, determined by cetyltrimethylammonium bromide (CTAB) absorption and by the oil absorption number (OAN). The CTAB value measures the specific surface area of silica that is accessible to the polymer chains. For the OAN measurement, di-(2-ethylhexyl) adipate (DOA) is used to fill the void volume of silica (the space between the solid particles) and refers to the structure of the silica. These crucial properties of silica highly influence the performance of rubber compounds and vulcanizates.[3] Moreover, two types of silica have been developed for better material handling purposes during mixing and storage, referred to as granulate and micro-pearl forms.

In general, silicas are divided into two groups: conventional silica (CV) and highly dispersible silica (HD). The main differences between these categories are their structures. The three-dimensional clusters of HD silicas have greater void volume (referred to as high structures) compared with CVs.[3,4,5] It has been reported that the macro-dispersion of silica and filler-rubber interaction in rubber compounds can be improved by this high-void volume. This was explained by the higher possibility for rubber molecules to penetrate into the voids of the silica clusters, resulting in higher rubber-filler interactions.[4,5]

Therefore, it is worth paying attention to elucidating how the raw forms (granulate and micro-pearl), structure and specific surface area of silicas influence the overall performance of rubber tread compounds. In this study, various commercially available silica grades were investigated. Different forms of silicas along with varying DOA and CTAB values were chosen to address these questions. Their influence on the dynamic and mechanical properties of the compounds were evaluated.

Materials

The following materials were used in this study:

- Different types of silica as presented in Table 1;
- Rubbers: S-SBR Sprintan SLR 4601-Schkopau, a solution styrene-butadiene rubber with 50 MU [ML(1+4) at 100°C] produced by Synthos, Germany; Buna CB24, a high-cis neodymium-catalyzed butadiene rubber with 44 MU [ML(1+4) at 100°C] produced by Arlanxeo Performance Elastomers, the Netherlands;
- Processing oil: Treated distillate aromatic extract (TDAE) oil, produced by Hansen & Rosenthal, Germany;
- Silane coupling agent: Bis-triethoxysilylpropyl tetrasulfide (TESPT, Si 69) with a sulfur content of ca. 22wt%, produced by Evonik Industries, Germany;
- Curing agents: Zinc oxide produced by Merck, Germany; sulfur by Eastman, USA; N-tert-butyl-benzothiazole sulfonamide (TBBS); and diphenylguanidine (DPG) produced by Flexsys, Belgium;
- Antioxidants: N-(1,3-dimethylbutyl)-N'-phenyl-p-phenylenediamine (6PPD)

Table 1: Analytical properties of silicas as well as the notations of different compounds prepared in this study

Silica code:	CTAB[1] Surface area (m^2/g)	DOA[2] Structure (g/100g)	Type of silica
CTAB_80_DOA_221	80	221	HD (GR[3])
CTAB_110_DOA_220	110	220	HD (MP[3])
CTAB_160_DOA_185	160	185	CV (GR)
CTAB_160_DOA_205	160	205	HD (GR)
CTAB_160_DOA_223	160	223	HD (MP)
CTAB_176_DOA_223	176	223	HD (MP)
CTAB_195_DOA_198	195	198	HD (GR)
CTAB_200_DOA_no data	200	no data	HD (MP)
CTAB_250_DOA_no data	250	no data	HD (MP)

[1]CTAB is the cetyltrimethylammonium bromide adsorption to measure the specific surface area of silica
[2]DOA is di-(2-ethylhexyl)adipate adsorption to assess the silica structure
[3]GR are granulates, MP are micro-pearls

produced by Flexsys, Belgium; stearic acid by Merck, Germany; and paraffin wax by Sasol, South Africa.

Experimental

The compounds were prepared in an internal mixer (Brabender Plasti-Corder 350S, Brabender, Germany) with a mixing chamber of 390ml. The fill factor was 70%. The mixing procedure is shown in Table 2. After stages 1 and 2, the compound was milled for five minutes on a two-roll mill (Schwabenthan Polymix 80T, Schwabenthan, Germany). In the third stage, the curatives were added on a two-roll mill, sheeted out and kept overnight before vulcanization and characterizations.

Cure characteristics of the compounds were measured using a Rubber Process Analyzer (RPA2000, Alpha Technologies, USA). The change in torque (S') of a compound at 160°C, frequency of 1.667Hz and 6.98% strain was measured for 20 minutes. The optimum curing time at 95% vulcanization degree (t_{95}) was used for curing the compounds.

Payne effect measurements were carried out using the RPA2000 with uncured rubber samples. The storage modulus (G') of the samples was measured using a strain sweep in the range of 0.56-100% with a frequency of 0.5Hz at 100°C.

Bound rubber measurements were carried out using an extraction method with and without ammonia treatment. The following procedure was applied:

- 0.2g of an uncured compound (without curatives) weighed using a four-decimal analytical balance. The sample was cut into multiple tiny pieces, placed into a filter bag made from a steel wire net with 300 mesh, and then immersed in toluene solvent for 72 hours at room temperature. The toluene (min. 98%, VWR Chemicals BDH, USA) was renewed every 24 hours;
- The sample was removed from the toluene and dried in a vacuum oven (Gallenkamp Vacuum Oven, vacuum level 10-6 Torr, UK) for 24 hours at a temperature of 60°C;
- The sample was immersed again in toluene for 72 hours at room temperature in either normal or ammonia (28-30%, Sigma-Aldrich, USA) atmosphere in order to cleave the hydrogen bonds and weak interactions between filler-filler and filler-rubber. The toluene was renewed every 24 hours;
- Finally, the sample was dried in a vacuum oven for 24 hours at 60°C. Then, the dried sample was checked on the analytical balance for its final weight.

Table 2: Mixing procedure

Stage 1	
Internal mixer Rotor speed: 75rpm Initial temperature: 50°C	
Timing (minutes:seconds)	**Action**
00:00	Add polymers
00:20	Close ram
01:20	Add ½ silica, ½ silane, ½ oil, ZnO, stearic acid, wax and 6PPD
01:50	Close ram
02:50	Add ½ silica, ½ silane, ½ oil
03:30	Close ram
04:30	Sweep
06:45	Discharge
0:00 – 5:00	Mix and sheet on a two-roll mill

Stage 2	
Internal mixer Rotor speed: 90rpm Initial temperature: 50°C	
Timing (minutes:seconds)	**Action**
00:00	Add the discharged compound obtained from the first stage
05:00	Discharge
0:00-5:00	Mix and sheet on a two-roll mill

Stage 3	
Two-roll mill Temperature: 50°C	
0:00-7:00	Add curatives

The following equation was applied in order to calculate the bound rubber content:

$$Bound\ rubber\ content\ (\%) = \frac{W - Wf}{Wp} \times 100$$

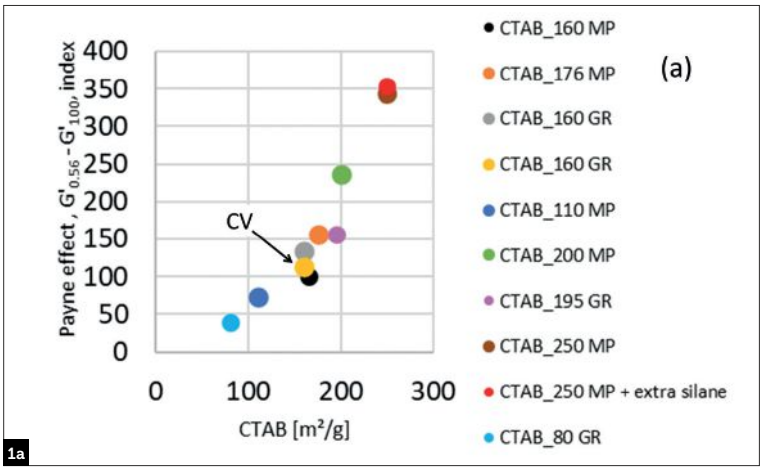
where *W* is the weight of silica with bound rubber or the weight of a sample after toluene extraction, *Wf* is the weight of the silica fraction in a compound, and *Wp* is the weight of the polymer fraction in a compound. These latter two were calculated based on the compound formulation and initial sample weight.

To assess tensile properties, the cured rubber sheets with a thickness of about 2mm were die-cut into dumbbell-shaped specimens (type S2) according to ISO 37:2011 using a Zwick/Roell Z1.0 tensile tester (Germany).

Dynamic mechanical analysis was also undertaken to study viscoelastic properties. This analysis utilized a Metravib DMA +450 (Metravib, France) with a double shear mode analysis.

Results

The present study addresses the importance of the impact of different types of silica on the performance of tire tread compounds. Various silica grades were selected for this comparison study to elucidate the influences of their technical properties, including: 1) The specific surface areas and structures; 2) The conventional versus highly dispersible grades; and 3) The granulate versus micro-pearl forms.



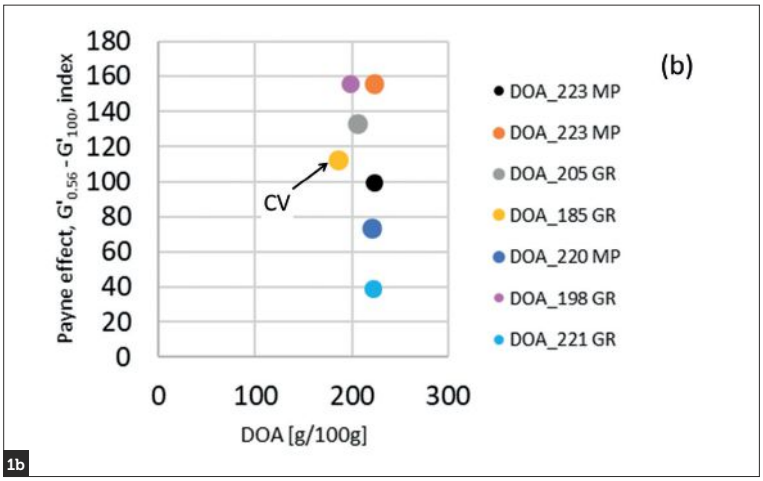


Figure 1: Payne effect of tire tread compounds filled with different silica grades as functions of CTAB (a) and DOA (b) values of silica

The results are appraised to elucidate the material characteristics related to the three specific influential aspects of the investigated silicas. All result values are assigned 'value indices', not performance indices, where a higher index indicates a higher measured value. The silica with a CTAB surface area and DOA structure of 160m²/g and 223g/100g, respectively, is used as the reference, with all presented properties assigned as an index value of 100.

Reinforcing parameters: filler-filler and filler-rubber interactions

Figure 1 demonstrates the filler-filler interaction, indicated by the Payne effect (difference of G' at 0.56% at G' at 100%), as a function of specific surface area (CTAB) as well as structure (DOA) of silica. A clear correlation between the specific surface area of the silica and the Payne effect of the compounds is observed (Figure 1a). Such a linear correlation cannot be found between the Payne effect and the silica structure (DOA) (Figure 1b). The filler-filler interaction significantly increases with increasing specific surface area or with smaller primary particle sizes of the silica. After dispersion/distribution of the silica in the compounds through an appropriate mixing, the smaller primary particles forming a cluster can more easily form a path throughout the rubber compound, attributed to the shorter interim distances between the different clusters. This filler network is facilitated by the strong polar affinity among the silica clusters by nature, as the silica surface contains a significant concentration of hydroxyl groups.[3,4,5] Thus, this phenomenon results in a higher density of filler network formed inside the compounds, which results in the higher observed Payne effect. For this reason, the Payne effect is also considered as an indicator of the microdispersion of the silica.[6]

The silica with a surface area of 250m²/g strongly aligns with the above explanation; even when an extra amount of silane was added to this compound (refer to CTAB_250 MP + extra silane), the filler-filler interaction has not changed. Therefore, it is recommended that the mixing parameters for the silicas with a rather high specific surface area should be fine-tuned, so that their microdispersion and the consequent final properties of the compounds can be improved.

Concerning the influence of silica structures (DOA), there is no clear correlation observed between the structures of silica and the Payne effects. Possible reasons are discussed later after the evaluation of other in-rubber properties.

When comparing the silicas with a given specific surface area of 160m²/g, but higher structures for HD grades (205g/100g and 223g/100g), the CV type exhibits a slightly higher filler-filler interaction compared with the HD micro-pearl type, but slightly lower than the HD granulate form. The HD micro-pearl even has a higher structure than the HD granulate and CV grades; however, it renders a lower filler-filler interaction. Compared with other silica grades, these three silicas have a similar filler-filler interaction.

Bound rubber content of the investigated compounds shown in Figure 2 shows the total bound rubber index, which includes the chemical and, to a significantly lesser extent, the physical rubber-filler interactions. The total bound rubber content correlates well with the specific surface area or CTAB values of silica (Figure 2). Aligning with the reasons given in the Payne effect part (Figure 1), the silicas with higher specific surface areas exhibit smaller primary particles in the clusters, providing a larger surface area when dispersed in a compound, resulting in a greater overall concentration of available hydroxyl groups to chemically interact with the silane coupling agent and the polymer chains. Consequently, the higher the specific surface area, the higher the rubber-filler interactions or bound rubber content.

When increasing the structure of silica (Figure 2b), an independence of the bound rubber content from the silica structure is observed, which is in line with the Payne effect results (Figure 1b). This issue is discussed later after appraising the overall properties.

Comparing CV and HD types with a given specific surface area of

160m²/g but higher structures for all HD grades, the CV type gives moderate filler-rubber interaction compared with its HD counterpart in granulate and micro-pearl forms. The HD micro-pearl promotes slightly higher rubber-filler interaction than that of the HD granulate. Nonetheless, it is consistent with the filler-filler interaction, when compared with other silica grades, that these three silicas provide similar filler-rubber interactions. This shows that the surface area of silica overshadows the effect of the difference in silica forms.

Based on the results of filler-filler and filler-rubber interactions (reinforcing parameters) demonstrated in Figures 1 and 2, changing from CV to HD or to higher-structure silica with the same specific surface area does not significantly influence these reinforcing parameters. The results obviously depict the strong influences of the specific surface area of silica on the reinforcing parameters. Ideally, a highly reinforced compound should comprise low filler-filler interactions and high filler-rubber interactions. When increasing the specific surface area, a higher filler-rubber interaction is implemented, but inevitably accompanied by an undesired higher level of filler-filler interaction. These two reinforcing parameters need to be balanced in silica-filled compounds. The following section discusses their influences on the vulcanizate properties.

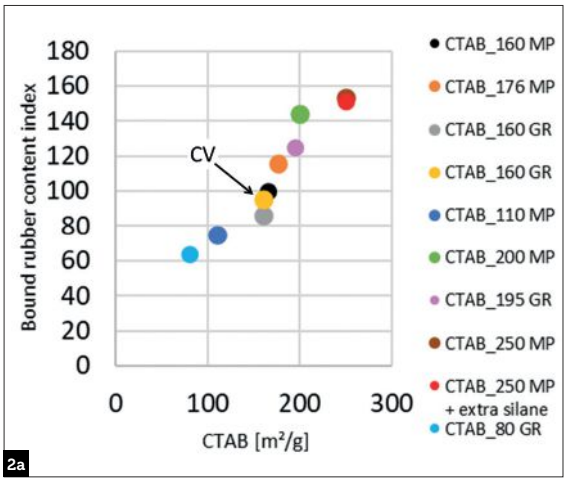
Final properties of the tire tread vulcanizates

Figure 3 (overleaf) shows the strength property of the investigated vulcanizates based on different silica types. The highest levels for both tensile strength and elongation at break are achieved for silicas with a specific surface area (CTAB) ranging from 110-200m²/g. The use of the silica with 80m²/g and the two silicas with 250m²/g in the compound does not enhance the mechanical properties as well as the others. This result can be explained by the earlier elucidation concerning the imbalance or competitive impact between filler-filler and filler-rubber interactions. Higher filler-rubber interactions lead to a higher strength of the vulcanizates, since the interfacial interactions enhance the homogeneity of the composites and enable a better force transmission inside the materials. This effect can be seen from the silicas with 110-200m²/g surface area. Additionally, the filler-rubber interaction also improves the elongation at break to a certain extent, despite the fact this factor makes the materials stiffer. Stronger interfacial interactions slightly prevent the breakage of the materials on a molecular scale at the filler-rubber interfaces since the weak spots are primarily originated at the interface between silica and rubber. However, when the filler-filler interaction is excessively high, giving a very poor microdispersion, the strength and elongation at break significantly drop, as can clearly be seen from the compound with the 250m²/g silica. This phenomenon is typically observed in 'reinforcing fillers'.

Considering the silica with a low surface area, 80m²/g silica (relatively lower when compared with other grades), this gives a lower active surface area while being dispersed in the compound, and the consequently lower levels in filler-filler and filler-rubber interactions as discussed in the previous part. Thus, this grade acts more like a semi-reinforcing filler, which exhibits the lowest mechanical properties in this comparative series.

The silica with 110m²/g provides rather high mechanical properties in comparison with the silicas with 160-200m²/g, in both strength and elongation at break. The silica with a CTAB surface area of 110m²/g has an HD micro-pearl form with a DOA number of 220g/100g. This might reflect that the silica structure shows its impact only when the specific surface area is low, since it can improve the final mechanical properties to a similar level as the higher surface area grades. This silica with a lower surface area but high structure presents its advantage over the other higher surface area grades in terms of its significantly low filler-filler interaction, implying easier processability. However, the silica with an 80m²/g specific surface area and a 221g/100g structure shows a substantially lower reinforcement efficiency. Thus, the CTAB surface area of 80m²/g is too low, even with a remarkably higher structure.

The CV silica shows lower strength and elongation at break indices compared with the HD ones with a given specific surface area of 160m²/g, implying that the increment of silica structure, to a lesser extent than the specific surface area, provides enhanced mechanical properties. Figures 3b and 3d show a clearly beneficial impact of silica structure when comparing the CV with other HD silicas with higher structures.



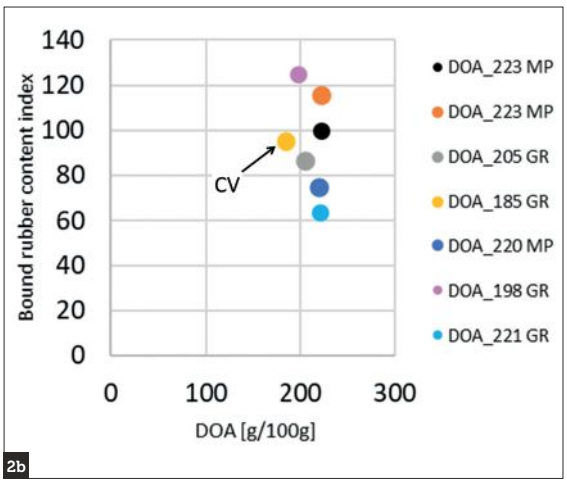
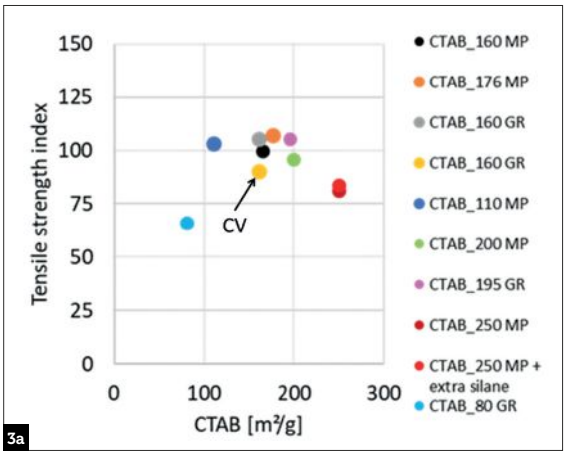


Figure 2: Bound rubber content of tire tread compounds filled with different silica grades as functions of CTAB (a) and DOA (b) values of silica

The loss tangent or tan δ at 60°C is taken as a laboratory indicator for tire rolling resistance, which is directly related to vehicle fuel consumption: the lower the rolling resistance, the lower the fuel consumption of vehicles.[5] Figure 4 (overleaf) illustrates the rolling resistance indicators of the investigated tire tread vulcanizates: the lower the index, the lower the rolling resistance.

The rolling resistance indicators are reduced by the silicas with increasing surface area from 160-200m²/g. The two silicas with the specific surface area of 250m²/g give a slightly higher rolling resistance indicator than the ones with 195m²/g and 200m²/g, which is again a sign of the imbalance between filler-filler and filler-rubber interaction. Based



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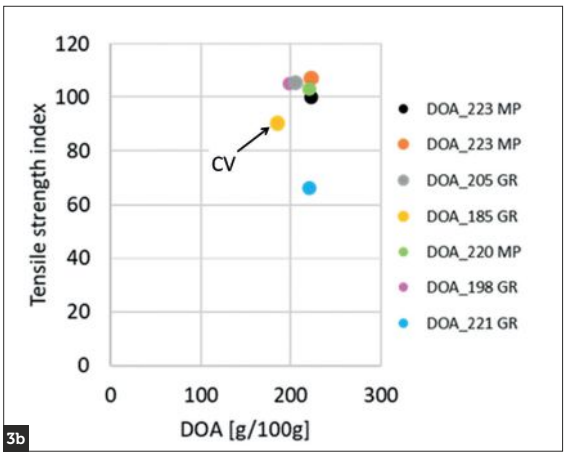

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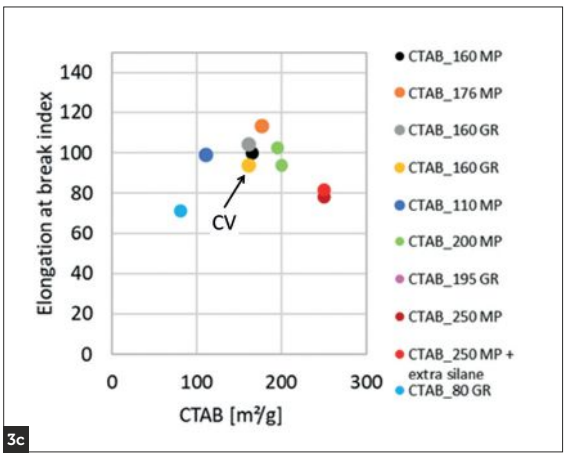

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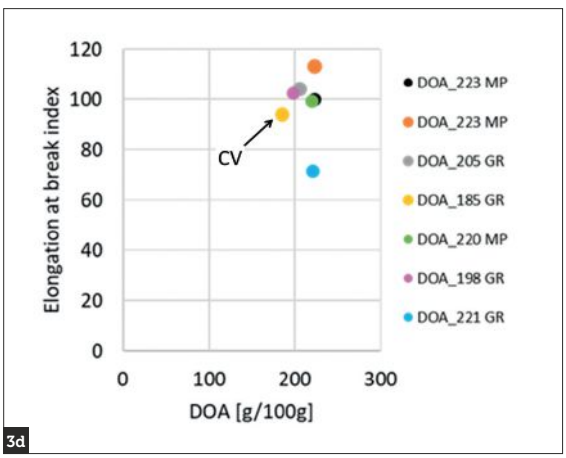


3d

Table 3: Compound formulations used in this study

Compounds	Quantity (phr)									
	1[3]	2	3	4	5	6	7	8	9	10
CTAB_160_DOA_223	90									
CTAB_176_DOA_223		90								
CTAB_160_DOA_205			90							
CTAB_160_DOA_185				90						
CTAB_110_DOA_220					90					
CTAB_200_DOA						90				
CTAB_195_DOA_198							90			
CTAB_80_DOA_221								90		
CTAB_250_DOA									90	90
TESPT[1]	7.20	8.16	7.63	7.87	5.25	9.54	9.54	3.82	11.93	13.72[4]
Sulfur[2]	1.40	1.30	1.35	1.33	1.61	1.15	1.15	1.76	0.90	0.71

All compounds contain the same amounts of these ingredients: S-SBR (75phr); BR (25phr); TDAE (32.5phr); Zinc oxide (2.5); TBBS (2.0); DPG (2.0); 6PPD (2.0); Stearic acid (1.0); Wax (1.5phr)

[1]TESPT amounts were adjusted according to the specific surface area of silica
[2]Sulfur amounts were adjusted to maintain the same active sulfur content in the whole compound
[3]Reference compound
[4]15% more silane was added, compared with Compound 9, based on the recommendation of the supplier. The name of this compound is CTAB_255_DOA + extra silane

on this, it can be considered that the filler-rubber interaction has the dominant effect on the dynamic properties of the final vulcanizates, as the higher elasticity indicated by a lower tan δ is achieved for silicas with 195m²/g and 200m²/g, despite the significantly greater filler-filler interaction or Payne effect in these compounds. With the lesser impact of the filler-filler interaction factor on the dynamic properties, the highest surface area silicas (250m²/g) exhibit a slight decrease in rolling resistance performance (a slight rise in tan δ at 60°C) compared with the 195m²/g and 200m²/g silicas.

For the silica with an 80m²/g surface area and a 221g/100g DOA structure, the vulcanizate has a substantially lower rolling resistance indicator compared with all the others. The mechanical properties are also considerably low for this silica grade, confirming the lesser reinforcing power due to its significantly low specific surface area, despite its relatively high structure. The low reinforcing efficiency of this grade is mainly due to the low filler-rubber interactions, even though it gives the lowest filler-filler interaction.

The dynamic properties of the vulcanizates when filled with different forms of silica – CV and two HD silicas with a given specific surface area of 160m²/g, but higher structures for HD grades – illustrate that the CV gives a slightly lower tan δ at 60°C, implying a slightly better rolling performance (or improved fuel consumption) for a tire tread compound. When compared with other compounds in the series, these three comparative compounds show a group of comparable data: the highest mechanical strength (Figure 3) but the lowest rolling performance indicator (Figure 4). This again supports the earlier statement that the filler-rubber interaction is the most influential factor in the dynamic properties of the rubber.

Concerning the granulate and micro-pearl forms of silica with a similar structure and specific surface area, the final properties demonstrate no significant DOA difference between these two forms. This is also valid for the data from the compound properties regarding filler-filler and filler-rubber interaction (reinforcing parameters) (Figures 1 and 2). Therefore, these findings confirm that the micro-pearl form would give the only benefit in terms of material handling as it has a minor fluffy character. When a micro-pearl silica is transported into the mixer, the fine content is significantly lower compared with the granulate counterpart.

Unclear relationship between silica structure and tire tread performance

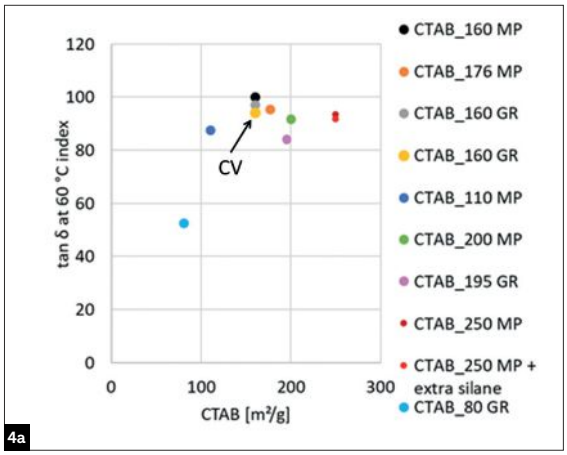
The specific surface area of silica determined by the CTAB method

appears to be the most influential factor on the in-rubber properties of tire tread compounds, while the silica structures in the range of 198-223g/100g, measured by the DOA technique, show scattered data when increasing the DOA number. However, if compared with CV and HD silicas with a given specific surface but a higher structure in the HD form, the essential impact of the higher structure is noticeable. It is important to remark that this study used only one type of CV silica, making it challenging to draw a solid conclusion.

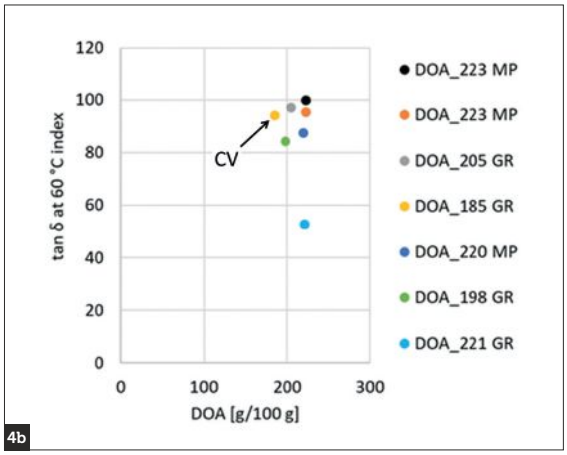
Regarding the structure of silica, it was expected that a higher structure relative to a higher void volume inside the silica clusters would lead to a better microdispersibility and a significantly higher filler-rubber interaction. This is because the polymer chains may effectively interact with the filler by penetrating into the micro-voids of the silica clusters.[7] However, the results in this work, to some extent, do not follow this concept. Based on the literature, compared with the structures of carbon black and silica with a given surface area, the morphology of a primary silica cluster exhibits less or non-branched structure, unlike carbon black aggregates. Silica clusters form a 'dense fractal structure' with micro-voids inside, while carbon black exhibits expanded aggregates due to the higher branched structure.[7,8] This is because silica has a high concentration of polar hydroxyl groups on its surface, which tend to form strong hydrogen bonding among the clusters.[3] This is why a branched structure cannot be referred to as silica clusters. The same is valid for the terminologies 'aggregate and agglomerate', which cannot be applied to the silica morphology as it is different from that of carbon black. With these differences between the structures of silica and carbon black due to the stronger affinity among silica primary clusters, the silica structure does not clearly influence the in-rubber properties as observed with carbon black. Additionally, the surface chemistry of the silica particles must be considered as well. This additional factor is not considered when only the void volume by DOA number is measured. Therefore, a clear correlation between the structure and the in-rubber properties cannot be found. This is exceptional when the specific surface area of silica is low (for example, 110m²/g); in this case, the higher silica structure shows a positive effect on enhancing the rubber performance.

Figure 3: Tensile strength and elongation at break of tire tread vulcanizates filled with different silica grades as functions of CTAB (a and c) and DOA (b and d) values of silica

Figure 4: Loss tangent at 60°C of tire tread vulcanizates filled with different silica grades as functions of CTAB (a) and DOA (b) values of silica



4a



4b

Conclusions

The CTAB specific surface area of silicas shows a clear influence on the compound and final in-rubber properties of tire treads. The DOA structure of silicas in this series does not significantly influence the tire tread properties, except when the specific surface area of silica is low (for example, 110m²/g), then the high structure of the silica exhibits an essential impact. CV silica gives inferior mechanical properties but comparable dynamic mechanical properties compared with its HD counterpart with a similar CTAB surface area but higher structure. The micro-pearl silica shows no significant difference with regard to the in-rubber performance of tread compounds, compared with the granulate silica. For the silicas with high CTAB specific surface areas, the mixing conditions need to be adjusted to reach a better dispersion level. Only then can these silicas be compared with the other silica types, and will they show their full potential. The dominant phenomena that competitively influence the properties of tire tread compounds include filler-filler and filler-polymer interactions. It is most likely that the filler-rubber interaction plays a dominant role in improving the dynamic properties of the rubber treads over the filler-filler interaction. **tire**

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