COMPARISON AND EVALUATION OF DIFFERENT ANALYTICAL METHODS TO PREDICT THE IN-RUBBER DISPERSIBILITY OF SILICA

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Abstract

The aim of the present investigation was to find a correlation between one single analytical parameter of precipitated silica and its in-rubber dispersibility. Therefore, 25 different types of silica with a variety of analytical parameters and dosage forms were investigated by means of standard analytical methods (CTAB, BET, DOA, pH and moisture content) as well as two new methods, the sedimentation test and the in-situ cluster fragmentation. Moreover, all types of silica were mixed inside a typical Green Tire formulation filled with 80 phr of silica. The macro-dispersion quality was evaluated by means of two dispersion measurement systems, the Topography where the surface roughness of a rubber sample is scanned mechanically by a probe and the Dispertester where the sample is investigated by an optical light microscope.

No significant linear correlation between the standard analytical parameter and the macro-dispersion quality could be found whereas the sedimentation method and in-situ cluster fragmentation provides promising approaches. However, it was not possible to directly predict the in-rubber dispersibility of silica by means of one single analytical parameter with a very high correlation coefficient.

Finally, different aspects which limit the general approach were discussed. Taking all these facts into account it becomes obvious that a linear correlation of one single analytical parameter with the dispersion quality cannot be found.

Introduction

Nowadays, precipitated silica in combination with bi-functional organosilanes are one of the most important fillers for passenger car tire tread compounds. This filler system leads, in combination with a special polymer system, to a better wet traction and lower rolling resistance in comparison to carbon black filled treads. However, the challenge is to reach a sufficient abrasion resistance as well. Therefore, a good dispersion and distribution of the silica in the rubber matrix is required. The filler itself has a great impact on the in-rubber dispersion quality. To support the development of new tailor-made highly dispersible silica it is crucial to be aware of the typical analytical silica parameters and their impact on the dispersibility. The term "dispersibility" describes the relative ability of fillers to be dispersed in a rubber matrix. The specific surface area (SSA) of silica for example influences the filler-filler, the polymer-filler interaction and therefore the in-rubber dispersion quality. However, up to now, no direct correlation between one single analytical parameter like the SSA and the dispersion behavior of the silica is known. For that reason, different analytical standard as well as new methods were investigated to predict the in-rubber dispersibility of silica by an analytical parameter.

In first place, 25 different types of silica with a variety of analytical parameters and dosage forms were investigated by means of the standard analytical methods CTAB, BET, DOA, pH and moisture content.

Moreover, all types of silica were investigated by means of a modified sedimentation method [1]. The measurement system is based on the settlement of silica clusters inside a water suspension after an ultrasonic pre-treatment. The heavier the particles the faster they settle. The particle size distribution is measured via X-ray absorption. With known viscosity of the fluid and known density of the fluid and of the silica, the spheres' diameters are calculated by the use of Stokes' law. It is expected that a highly dispersible silica containing smaller clusters can be distinguished by this method from a conventional silica containing larger particles.

Another approach to predict the in-rubber dispersibility of silica is the use of the in-situ cluster fragmentation which derived from the lasergranulometry measurement [2]. During the measurement a silica sample circulates in a fluid e.g. water loop. The suspension passes an ultrasonic device and thereby bigger clusters get fractured into smaller ones. The particle size and distribution are continuously measured over the measurement time via laser diffraction. Due to different interactions between the laser beam and the particles (diffraction, refraction, reflection & absorption) a scattering pattern is generated. In this way the decrease of clusters can be recorded over a certain time. The principle idea is that the easiness of the cluster breakage can be a measure for the dispersibility of the silica in the rubber matrix.

All types of silica were mixed inside a typical Green Tire tread formulation filled with 80 phr of silica. The macro-dispersion quality was evaluated by means of two dispersion measurement systems, the Topography where the surface roughness of a cut rubber sample is scanned mechanically by a probe and the Dispertester where the sample roughness is investigated by an optical light microscopy. Finally, all results from the standard and new analytical methods are correlated with the macro-dispersion qualities in order to find a linear relation between these parameters.

Experimental part
Standard analytical parameter of silica
The dispersibility of silica can in general only be assessed within the same formulation, using the same mixing equipment and mixing process. To achieve various different dispersion qualities and broadening the results, a wide variety of silica types has therefore to be investigated. 25 different types of silica with a wide variety of analytical parameters were chosen. Three dosage forms can thereby be distinguished, granules (GR), powders (P) and micro-pearls (MP). The five standard analytical parameter of silica are specified: CTAB [3] and BET [4] to evaluate the specific surface area, DOA [5] to determine the initial structure of silica, pH-value [6] and moisture content [7].

All silica grades are labelled as follows: The first number represents the specific surface area measured by CTAB, the letter characterizes the dosage form and the last number describes the initial structure measured by DOA.

Sedimentation analysis
The sedimentation measurement (SediGraph III Plus by Micromeritics GmbH [8]) consists of a fixed X-ray source and a detector. In between these components a moveable vertical measurement cell is situated, connected to a tube system in which the sample solution can circulate (Fig. 1).
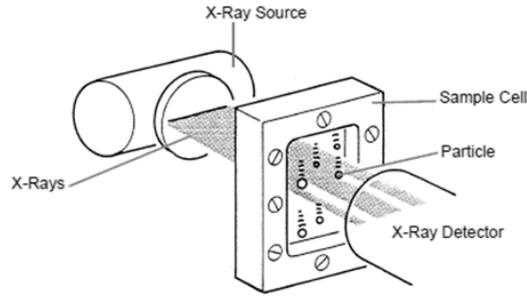
Figure 1: Schematic view of the sedimentation method including a filler sample [8]

During a measurement cycle, silica particles settle inside a water suspension by means of gravity. The heavier the particles are the faster they settle. The absorption of an X-ray beam (0.125 mm wavelength) by the silica clusters is measured. This is based on the Beer-Lambert law of extinction describing the extent to which the intensity of a beam is exponentially reduced by passing through an absorber. It is dependent on the absorption coefficient and the concentration of the suspension and the distance the beam has to pass. This special characteristic results in a benefit over optical light and laser-based measurement systems where next to the absorption also scattering, refraction and diffraction effects have to be taken into consideration. With known viscosity of the fluid, density of the fluid and density of the silica the spheres' diameters are calculated by the use of Stokes' law. It is expected that a highly dispersible silica containing smaller clusters can be distinguished by this method from a conventional silica containing larger particles.

The calculation of the particles sizes and distribution is based on the assumption that the equilibrium velocity of particles through a defined viscous medium can be related to the diameter of the particles (eq. 1) [9]:

$$D_s = K * v^{1/2} \qquad \textbf{(eq. 1)}$$

where:

$$K = \sqrt{\frac{18 * \eta}{(\rho - \rho_0) * g}} \qquad \textbf{(eq. 2)}$$

D_s represents the calculated sphere diameter in µm, K is a combination of constants, ρ is the fillers' density in g / cm³, which is for silica 2.0 g / cm³ [10], and v is the equilibrium sedimentation velocity of the particle in m / s. The fluid is characterized through its density ρ_0 in g / cm³ and viscosity η in Pa * s. The gravity g is given in m / s². The combination of eq. 1 and eq. 2 results in the Stokes' law equation (eq. 3):

$$D_s = \sqrt{\frac{18 * v * \eta}{(\rho - \rho_0) * g}} \qquad \textbf{(eq. 3)}$$

As a matter of fact, silica particles are irregular shaped and therefore do not meet the requirements for being described by a single linear dimension. Therefore, the term "Stokes' diameter" was introduced. It is defined as the diameter of a perfect sphere (identical material) that settle with the same sedimentation velocity as the actual particle. This assumption is very well accepted in practical use [8].

The suspension inside the measurement cell has the highest concentration of particles at the beginning of the measurement and therefore the lowest X-ray intensity is detected. During settling of particles the concentration decreases and the recorded X-ray intensity increases [11]. The particle size distribution is evaluated as shown in Fig. 2 where the concentration of particles (cumulative mass finer) is plotted against the calculated diameters.
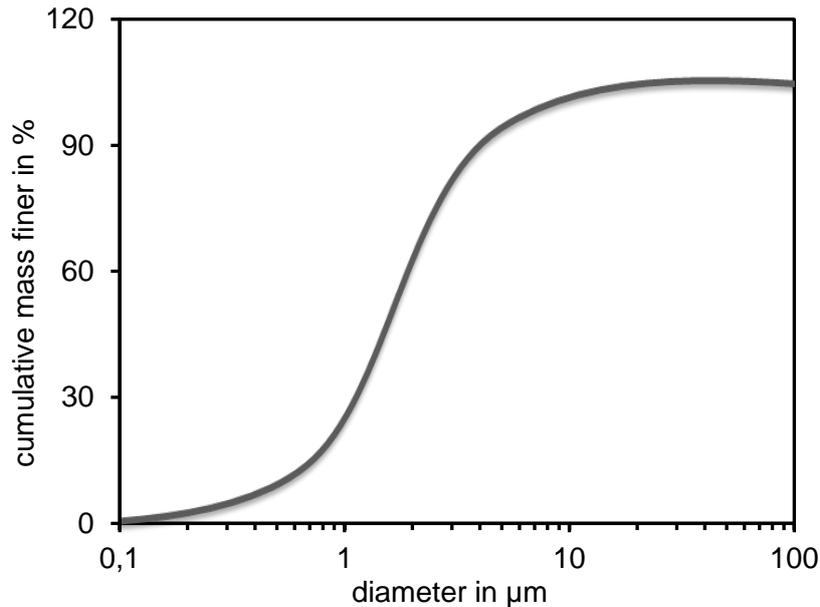
Figure 2: Typical particle size distribution curve measured by the sedimentation analysis

At the beginning of the measurement, when the concentration of particles is the highest, the cumulative mass finer is at 100 % which implies that no settling took place yet. Assuming all particles have settled and only pure fluid is left inside the measurement cell the cumulative mass finer reaches 0 % which corresponds to the measured baseline intensity. Due to the fact that the heavier the particles are the faster they settle, the biggest clusters are recorded at first. It is possible to detect particle sizes between 300 to 0.1 µm [8].

The most suitable sample preparation corresponds to the following [12]: An ultrasonic device (Branson Digital Sonifier 450D incl. a flat ½'' tip by BRANSON Ultrasonic Coop.) was used to treat a suspension of 50 ml of demineralized water and 5 g of silica for 4 min at an amplitude of 70 %. During the treatment the suspension was cooled in a water bath (beaker halfway immersed) at 5 °C.

Following machine parameters and settings are chosen to conduct the experiments [12]:

- Analysis Type: high speed
- Analysis Temperature: 35 °C
- Analysis Liquid   demineralized water
- X-Ray Intensity: Normal
- Density Silica: 2.0 g / cm³
- Concentration: 50 ml H_2O + 5 g silica
- Ultrasound: 70 % amplitude for 4 min in a cooling bath at 5 °C

The results of the sedimentation analysis (SG) were correlated to the in-rubber macro-dispersion quality of rubber compounds. Therefore, the values of particles **bigger than 2 µm** were recorded. This number corresponds to the distinction between macro- and micro-dispersion in accordance with the ASTM definition [13]. In addition, the amount of particles **bigger than 1 µm** were evaluated as well.

In-situ cluster fragmentation

During the in-situ cluster fragmentation measurement, the silica sample circulates in a closed water loop including three main elements (Fig. 3). The first part (1) is the laser diffraction measurement system (Mastersizer 3000 by Malvern Instruments Limited) itself which measures the particle size distribution. It consists of two laser light sources, a He-Ne-laser respectively red laser (632.8 nm wavelength) and a LED light source or blue laser (470 nm wavelength) [14]. The second component

(2) is the ultrasonic device (Branson Digital Sonifier 450D incl. a flat ½'' tip by BRANSON Ultrasonic Coop.) which is attached to a cooled (15 °C) continuous flow cell (Sonifier Cell Disruptor by BRANSON Ultrasonic Coop.). This cooling system is permanently turned on to prevent the system from heating up due to the heat transfer from the sonotrode. The last element (3) is a wet dispersion unit (Hydro SM by Malvern Instruments Limited) which ensures and controls the flow speed of the suspension.
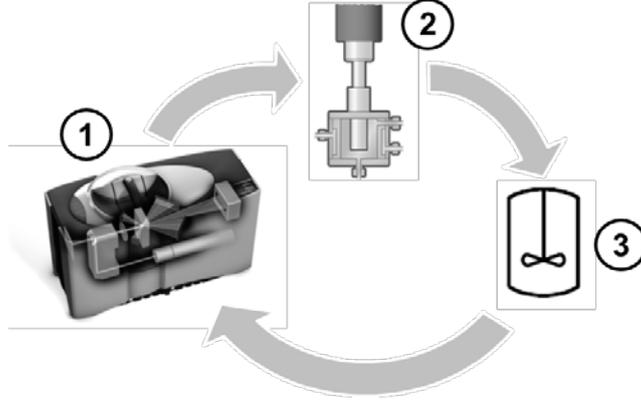

Figure 3: Schematic view of the measurement setup [14]

With this setup it is possible to continuously measure the particle size distribution respectively reduction over a period of time while being treated with ultrasound. The principle idea is that the easiness of the cluster breakage can be a measure for the dispersibility of the silica in the rubber matrix.

During the measurement, the laser beams pass the measurement cell with the flowing suspension of silica and water. When a beam hits a particle different interactions and optical effects occur which have to be taken into account [15]: Absorption, scattering, diffraction, reflection, refraction, extinction and transmission. All these effects result in a scatter pattern which is recorded by a detector array surrounding the measurement cell in different directions (0.015 to 144 degree setup). Each specific diffraction pattern respectively scattering angle corresponds to a defined particle size in the range of 3000 µm down to 10 nm.

The systems includes a Fourier lens to ensure that all particles of an identical size are scattered to the same part of the detector array. By means of the obtained pattern the Mastersizer 3000 software calculates the volume based concentration of the sample by means of the Beer-Lambert law as expressed in equation 4:

$$T = \frac{I}{I_0} = e^{-\alpha_i * b} \qquad \textbf{(eq. 4)}$$

Where T is the relative transmission measured by the device, I represents the intensity of light at the distance b in mm inside the particle field, I_0 is the initial intensity of the beam measured without a sample and α_i is the absorbance. The latter includes information about volume based particle sizes and concentration as following:

$$\alpha_i = Q_i * \pi * r^2{}_i * n_i \qquad \textbf{(eq. 5)}$$

With Q_i representing the efficiency of the extinction of light for a particle radius r_i which can be calculated by different optical models. The cross-sectional area of the particle is given by $\pi * r^2$ and the total amount of particles is expressed by n_i. Taking the volume of particles V_i into account, equation 5 is adjusted for all particles inside the sample:

$$\alpha_i = \frac{3}{4} \sum \frac{Q_i * V_i}{r_i} \qquad \textbf{(eq. 6)}$$

When now expressing the particle size by the diameter d in µm and separating the volume term into a relative volume distribution v and the total concentration C_v, the equation is described as follows

$$\alpha_i = \frac{3}{2} C_v \sum \frac{Q_i * v_i}{r_i}$$

(eq. 7)

When finally substituting eq. 7 into eq. 4 the volume concentration for each particle size can be obtained [14]. The particle size distribution was calculated by using the Fraunhofer scattering theory used in accordance with ISO 13320 [15].

The test procedure was conducted as follows [12]: 150 ml of demineralized water was filled into the device. While the liquid circulated throughout the system the temperature was kept between 20 and 25 °C by means of the cooled (15 °C) continuous flow cell. Subsequently, 50 mg of the sample was added to the liquid through the opening of the dispersion unit and the test procedure was started. Every 10 s a new particle size distribution curve was recorded. In between each measurement, a 5 s break was conducted. The total measurement time corresponds to 6 min. During the measurement, the ultrasonic device was used in a pulsed way which means that it is turned on and off alternately (1 s on / 1 s off).

To evaluate the final results two different curve characteristics of each single obtained measurement curve were evaluated, the progression of the D[4;3] value and the Dv90 value. The **D[4;3]** value correspond to the volume weighted mean or De Brouckere mean, often simply called ''mean'' and is expressed as follows [16]:

$$D[4,3] = \frac{\sum_1^n D_{ivi}^4}{\sum_1^n D_{ivi}^3}$$

(eq. 8)

With D_{ivi} as the size for each measured diameter with a defined volume. This evaluation of the mean value was named the mean degradation rate. In addition, the **Dv90** value, which corresponds to the size where 90 vol% of the sample are smaller than the given diameter, was evaluated as well.

Fig. 4 depicts an example of the inverse mean progression of three different types of silica (161GR193, 165P196 and 157MP207) over the time.
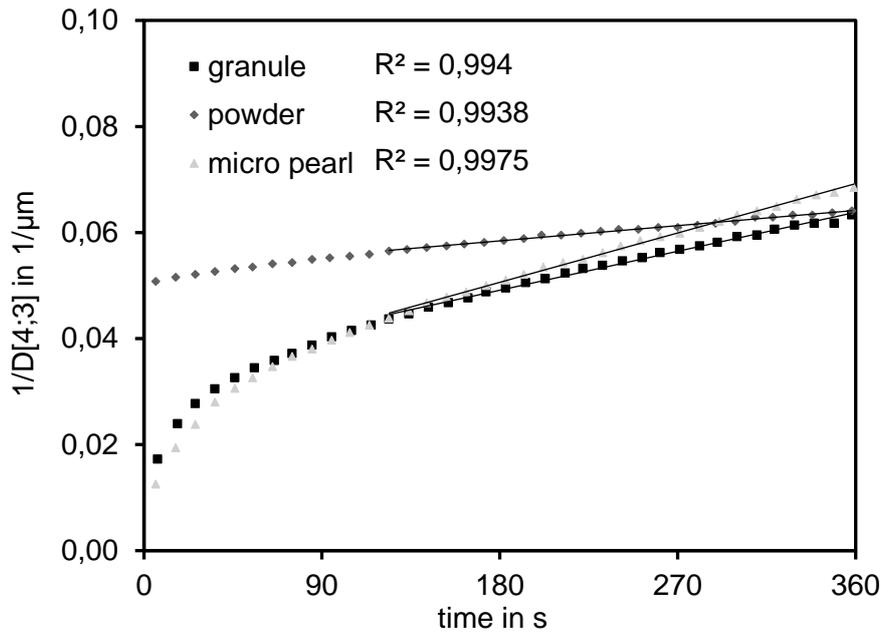
Figure 4: Evaluation of the mean value for one silica granule, powder and micro pearl

It can be seen that the coarser dosage form of granules and micro pearls show a non-linear slope in the first 1 ½ min whereas powders exhibit an almost steady gradient throughout the measurement. However, all three measured types of silica possess a high linearity (fitted regression line R^2) within 120 and 360 s. Therefore, the slope within this time frame was used to evaluate the speed of degradation. The comparable small calculated slopes (numerical values) can only be differed from the fifth decimal on. Therefore, all results were multiplied by 10^4 to deal with more manageable numbers. This adjustment does not affect the final outcome and was only made due to practical reasons.

The settings for all measurements are as described in the following [12]:

- Weight of sample: 50 mg
- Analysis temperature: 20 - 25 °C
- Analysis liquid: demineralized water
- Ultrasonic treatment: 100 % amplitude, pulsation (1 s on / 1 s off), 6 min
- Stirring speed: 3000 rpm
- Theory: Fraunhofer approximation
- Evaluation: slope between 2 and 6 min for the inverse parameters of Dv(90) and D[4;3], new measured distribution all 10 s

Compound formulation and mixing process

The used compound formulation is based on a typical Green Tire tread composition for passenger cars and includes 80 phr of silica and linear to the fillers' CTAB SSA adjusted silane amounts. The mixing process was divided into three stages and mixed inside a 1.5 l tangential mixer (Werner & Pfleiderer). The fill factor, rotation speed of the rotors and chamber temperature were set to a fixed level without being adjusted during mixing. After each mixing stage the compounds were sheeted out on a two roll mill (Schwabenthan 3.0 - Servitec Maschinenservice GmbH). Tab. 1 depicts the formulation used for this series.

Table 1: Green Tire formulation filled with 80 phr of silica (GT80)

1st stage

Material	type	phr
Buna VSL 4526-2	oil-extended S-SBR	96.25
Buna CB 24	Nd-BR; cis1,4 > 96 %	30.00
Silica	variable	80.00
Si 266	silane	adjusted to CTAB
N330	carbon black	5.00
ZnO RS RAL 844 C	zinc oxide	2.00
Edenor ST1 GS	stearic acid	2.00
Vivatec 500	TDAE* oil	8.75
Vulkanox HS/LG	TMQ** protector	1.50
Vulkanox 4020/LG	6PPD*** anti-aging	2.00
Protektor G 3108	Wax	2.00

2nd stage

batch 1st stage		
Rhenogran DPG-80	80 % DPG**** accelerator	2.50

3rd stage

batch 2nd stage		
Richon TBZTD OP	TBzTD***** accelerator	0.20
Vulkacit CZ/EG-C	CBS****** accelerator	1.60
Sulfur 80/90	soluble sulfur	2.00

*	TDAE:	Treated Distillate Aromatic Extracted
**	TMQ:	2,2,4-TriMethyl-1,2-dihydroQuinoline
***	6PPD:	N-(1,3-dimethylbutyl)-N'-Phenyl-p-PhenyleneDiamine
****	DPG:	N,N'-DiPhenylGuanidine
*****	TBzTD:	TetraBenzylThiuram Disulphide
******	CBS:	N-Cyclohexyl-2-BenzothiazoleSulfenamide

The amount of silane (Si 266) was adjusted to the specific surface area of silica (CTAB) to guarantee a sufficient hydrophobization of the polar surface of the filler. As a basis, the ratio of 5.8 phr silane to 80 phr of silica with a CTAB of 160 m² / g was chosen. The adjustment to other types of silica respectively CTAB surface areas was made by the rule of three. All other ingredients were kept constant so that differences in dispersion qualities should mainly be traced back to the analytical properties of the different types of silica itself. Tab. 2 shows the mixing process for the Green Tire tread series.

Table 2: Mixing process for the Green Tire tread compounds filled with 80 phr of silica

stage and time	action
1st stage min:sec	fill factor 0,73; 70 rpm; chamber temperature: 70 °C measured temperature: 130 -150 °C
00:00 - 00:15	polymer
00:15 - 00:45	1/3 silica; 1/3 silane
00:45 - 01:15	1/3 silica; 1/3 silane
01:15 - 02:15	a) oil adsorbed on CB in a PE pouch
	b) 1/3 silica; silane
	c) protector
02:15 - 04:15	ZnO, stearic acid; Vulkanox HS; Vulkanox 4020;
04:15	dump & control temperature
	45 s on open mill (4 mm nip), sheet out
	weigh compound for 2nd step; storage for 24 h / RT
2nd stage min:sec	fill factor 0,70; 70 rpm; chamber temperature: 90 °C measured temp.: 130 -150 °C
00:00 - 01:00	plasticize 1st stage
01:00 - 03:00	DPG; mix;
03:00	dump & control temperature
	45 sec. on open mill (4 mm nip), sheet out
	weigh compound for 3rd step; storage for 4 - 24 h / RT
3rd stage min:sec	fill factor 0,68; 55 rpm, chamber temperature: 50 °C measured temperature: > 110 °C
00:00 - 02:00	batch stage 2; accelerators; sulfur
02:00	dump batch; process on open mill 20 sec. with 3 - 4 mm nip
	cut 3 x left, 3 x right with 3 mm nip
	roll up & pass through a 3 mm nip x 3
	sheet off; store for minimum 12 h before vulcanization

Silica powders are in general more difficult to handle and to incorporate into the rubber during mixing in comparison to other dosage forms. Therefore, silica was added in three equal portions during the first stage. Fig. 5 depicts the fingerprint of the 1st stage of mixing for one type of silica (155P213) including the ram position, the power and the temperature profile as a function of time. The rotor speed was kept constant throughout the whole mixing.
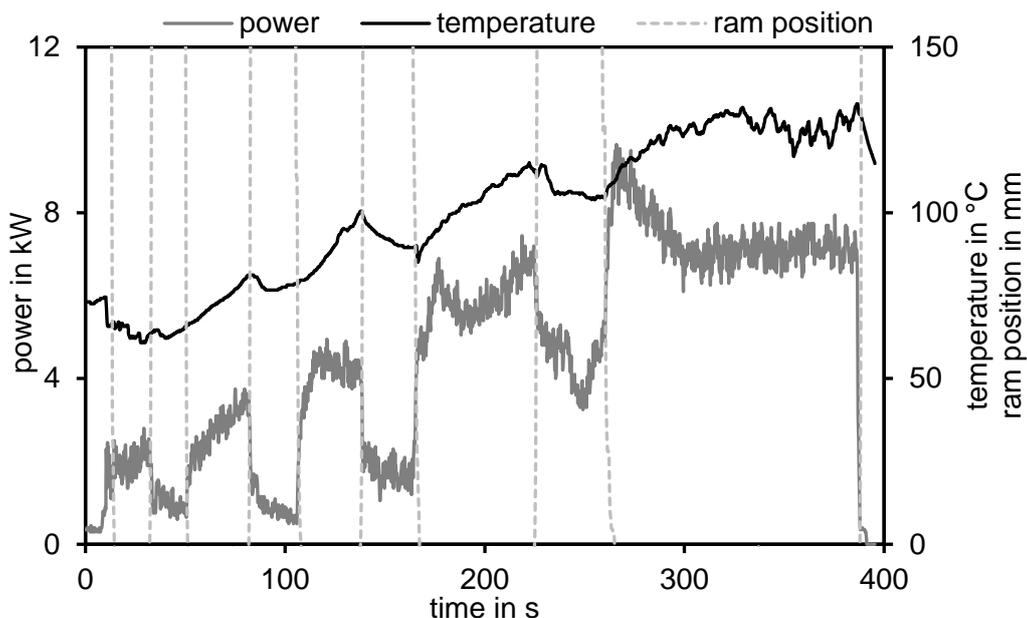
Figure 5: Fingerprint of the 1ˢᵗ stage of mixing for one type of silica (155P213)

It can be seen that by adding the filler in three parts the ram was able to quickly settle to its final position and mixing could be continued. After the addition of the 3ʳᵈ portion of silica including the other ingredients the power increased strongly due to the fact that the optimum fill factor for the mixing chamber was reached. During the last part of the mixing, the temperature reached an optimal level of +130 °C where the silanization reaction takes place without a risk of pre-scorch (average power of 7 kW). There was no need to adjust the rotor speed during mixing for any compound. Difficulties with the incorporation of silica respectively settling of the ram only occurred occasionally with the use of powders. All types of granules and micro-pearls were incorporated without any problems. The mixing of the stages 2 and 3 did not show any conspicuousness as well.

Dispersion measurement

The dispersion quality evaluations are conducted with vulcanized rubber samples. Therefore, the cure curves for all compounds were determined by means of a moving die rheometer (MDR by Alpha Technologies) at an oscillating shear angle of 0.5° and a frequency of 1.67 Hz in accordance with DIN 53529/ ISO 13145:2012 [17]. For each compound, the t95 time was evaluated. To keep to a consistent vulcanization time it was decided to use the respectively longest t95 value within the series for all samples. The following vulcanization condition was finally chosen: 15 min at 165 °C.

Topography

Based on ASTM D 2663 - Method C [18], the macro-dispersion quality was evaluated by applying the EVONIK Topography Test (Topo) which is a mechanical measurement method. This quantitative method is used to detect the surface roughness of rubber compounds. A freshly cut rubber surface is required for the measurement. While cutting the rubber specimen with a razor blade, the softer polymer is divided into two halves whereas the harder filler particles remain intact only on one side of the cut rubber sample. Consequently, certain irregularities (such as protrusions and depressions) will be created. The resulting roughness was scanned by a suitable probe and information about peak heights and the defected area were obtained [18-20]. Fig. 6 depicts the total amount of detected surface defects bigger than 2 µm in height as an example of the dispersion qualities obtained by the 25 different types of silica.
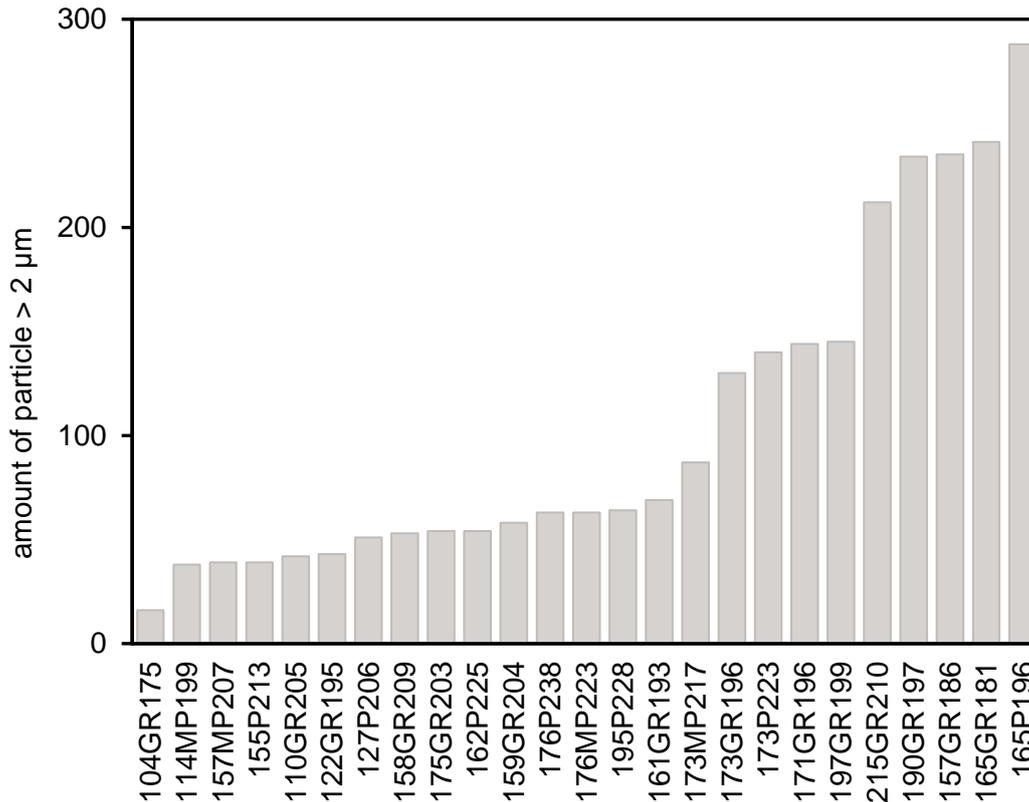
Figure 6: Obtained residual amount of detected surface defects bigger than 2 µm in height for 25 types of silica by means of the Topography measurement

It can be seen that the amount of detected surface defects bigger than 2 µm in height roughly differ from 15 up to 290. The less undispersed particles are detected, the higher the final macro-dispersion quality is.

Dispertester

The Dispertester is an optical measurement systems based on ASTM D7723-11, the "Standard Test Method for Rubber Property – Macro Dispersion of Fillers in Compounds". A cut rubber sample is investigated by an optical light microscopy with 30° irradiation angle and usually at 100x magnification. A Charge-Coupled Device (CCD) camera digitizes a grayscale image. The percentage dispersion of fillers was calculated by evaluating the white area related to the total scanned sample area. This white area is the scanned area that possesses surface defects caused by undispersed fillers. Additionally, the size distribution of detected surface defects was analyzed [21]. Fig. 7 depicts the variety of dispersion qualities obtained by means of the Dispertester.
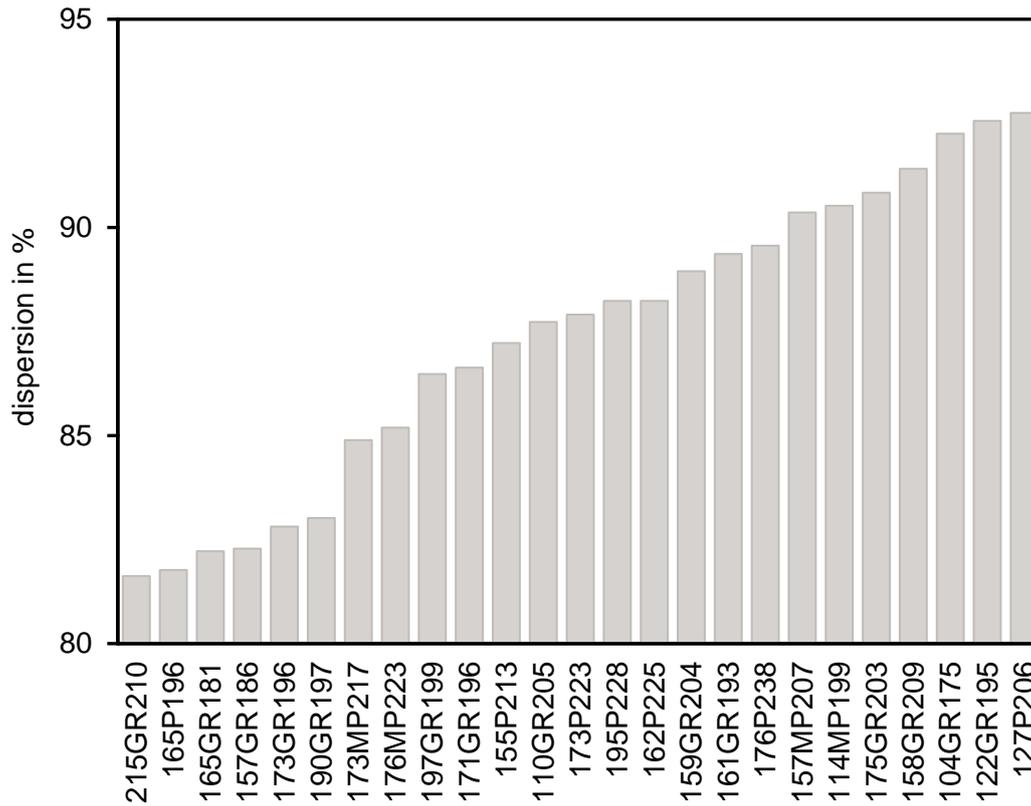
Figure 7: Obtained dispersion quality in % for 25 types of silica by means of the Dispertester measurement

As shown, the results of the dispersion measurements differ from roughly 81 to 92 %. The higher the dispersion in % is, the less undispersed particles were detected by means of the Dispertester and hence the better the macro-dispersion quality is.

Correlation between analytical parameter and in-rubber dispersion quality

In order to find a direct linear correlation between one single analytical parameter and the macro-dispersion quality of silica all analytical data sets and in-rubber dispersion measurements were compared with each other. Only when a sufficient high correlation is obtained, conclusions to the in-rubber dispersibility can be drawn. Therefore, the Pearson product-moment correlation coefficient *r* was determined for each possible combination of results. It describes a linear correlation between two sets of values *x* and *y* and is calculated as shown in eq. 9 [22]:

$$r = \frac{\sum(x-\overline{x})*(y-\overline{y})}{\sqrt{\sum(x-\overline{x})^2*\sum(y-\overline{y})^2}}$$ **(eq. 9)**

Where $\overline{x}$ and $\overline{y}$ are the mean values of the data sets. The values of the correlation coefficient *r* can vary between +1 and -1 whereby +1 correspond to the best possible positive and -1 to the highest possible negative correlation. A positive correlation means e.g. that the higher the value *x is*, the higher is the value *y*. Whereas a negative correlation means that the higher the value *x is*, the lower is the value *y*. In accordance with Evans [23] all values higher than +0.79 respectively smaller than -0.79 indicate a very strong dependency of both parameters to each other.

Correlation with standard analytical parameter

To begin with, the five standard analytical parameter of silica (CTAB, BET, DOA, pH and moisture content) were correlated with the dispersion qualities of all compounds obtained by Topography (peak area in % and the amount of defects bigger than 2 µm) and the Dispertester (dispersion in %). Tab. 3 depicts the calculated correlation coefficients.

dispersion	CTAB	BET	DOA	pH	moisture
peak area	0.44	0.45	-0.34	-0.57	-0.20
> 2 µm	0.49	0.49	-0.32	-0.54	-0.19
Dispertester	-0.57	-0.56	0.12	0.50	0.13

It can be seen that no direct linear correlation between one single standard analytical parameter of silica and the dispersion quality was obtained, all coefficients are even below 0.6. Therefore, it is not possible to predict the in-rubber dispersibility by means of one single standard parameter as stated in the introduction. Hence, the need for a new analytical parameter respectively measurement system is emphasized.

In addition to the correlation trials of the dispersion qualities with the standard analytical parameter, the dispersion measurement systems, the Topography and the Dispertester, were compared to each other (Tab. 4).

Table 4: Correlation coefficients of the Topography and Dispertester measurements

	peak area	> 2 µm
peak area		
> 2 µm	**0.99**	
Dispertester	**-0.83**	**-0.84**

It can be seen that the peak area and the amount of particles bigger than 2 µm show a high correlation coefficient. This is expected due to the fact that both parameters are determined by means of the Topography. Moreover, a correlation between the Dispertester measurement and the Topography is shown. In this case, the two different measurement principles lead to similar results.

Correlation with sedimentation method

The obtained evaluation parameter of the sedimentation method are the amount of residual particle (in %) left inside the suspension after the ultrasonic treatment which are bigger than 1 respectively 2 µm. These parameters were correlated with the dispersion qualities of all compounds obtained by Topography (peak area in % and the amount of defects bigger than 2 µm) and the Dispertester (dispersion in %). Tab. 5 depicts the calculated correlation coefficients.

Table 5: Correlation coefficients between the sedimentation analysis and both dispersion measurement methods

	peak area	> 2 µm	Dispertester
% particle > 1 µm	0.63	0.69	-0.76
% particle > 2 µm	0.69	0.74	**-0.77**

It is shown that the determined correlation coefficients are higher in comparison to the coefficients obtained by means of the standard analytical parameter (Tab. 3). However, a direct linear correlation could not be achieved. A best result was found comparing the Dispertester dispersion qualities (dispersion in %) with sedimentation values (% of particles bigger than 2 µm). Fig. 8 depicts the linear correlation of both measurements.
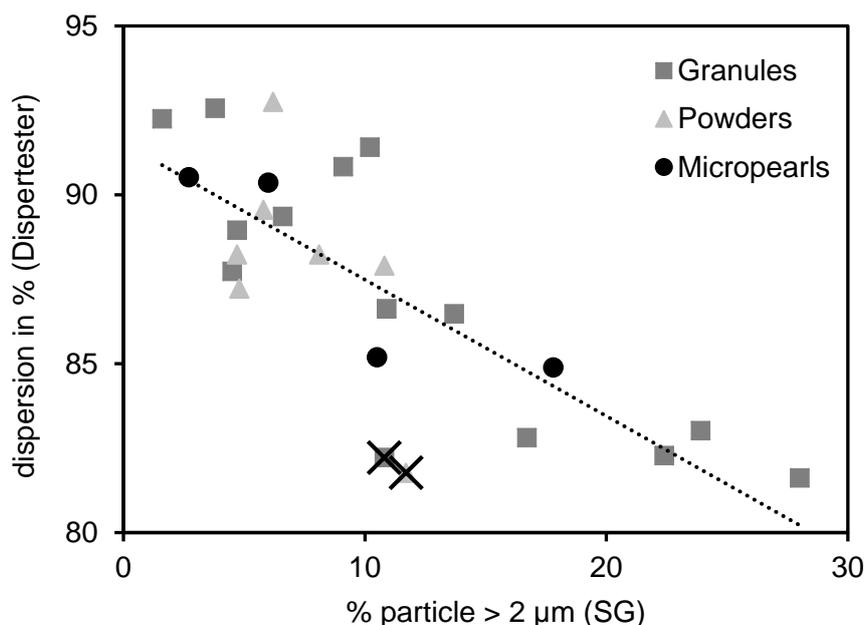
Figure 8: Linear correlation between the dispersion quality (Dispertester) vs. sedimentation values (SG)

It can be seen that the overall correlation seems to be sufficient with the exception of two values having roughly 10 % of the amount of particles bigger than 2 µm (SG) but exhibiting a disproportionate high amount of undispersed particles measured by means of the Dispertester (marked in Fig. 8 by an "X"). Neglecting both values inside the correlation, the coefficient of -0.77 increases to a value of -0.85. These two types of silica are related to each other in a sense that these are the powder and granule form of the same precipitation. As a matter of fact, both fillers were produced by a special process which differs from the other 23 samples. However, the requirement to the analytical method being universally valid for all types of precipitated silica cannot be fulfilled by this technique.

Correlation with in-situ cluster fragmentation
The in-situ cluster fragmentation was evaluated by means of the progression of two parameters, the mean degradation rate and the Dv90 values. These parameters were correlated with the dispersion qualities of all compounds obtained by Topography (peak area in % and the amount of defects bigger than 2 µm) and the Dispertester (dispersion in %). Tab. 6 depicts the calculated correlation coefficients.

Table 6: Correlation coefficients between the in-situ cluster fragmentation and both dispersion measurement methods

dispersion	D[4;3]	Dx(90)
peak area	-0.68	-0.69
> 2 µm	-0.72	**-0.73**
Dispertester	0.68	0.68

The best correlation coefficient found within these compounds was the Dx(90) progression as a function of the amount of particles bigger than 2 µm measured by means of the Topography. To see if any indications to the in-rubber dispersibility of silica can be concluded, this data set was plotted in the following way (Fig. 9):
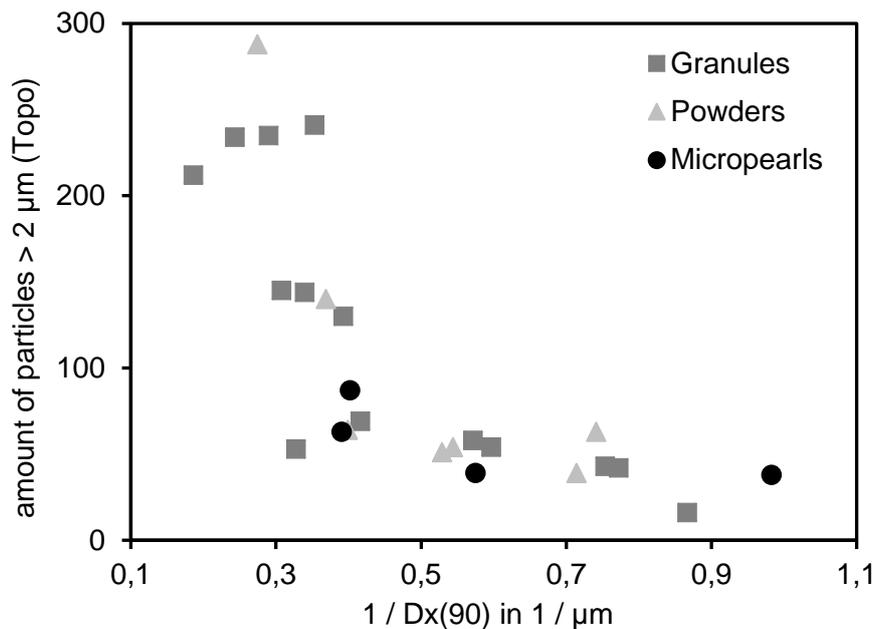
Figure 9: Correlation between the Dx(90) progression value and the amount of particles bigger than 2 µm measured by means of the Topography

It can be seen that the obtained values possess a pronounced exponential relation instead of a linear correlation. As a matter of fact, this relation cannot be calculated by means of the Pearson product-moment correlation coefficient *r* which takes only linear correlations into account [22]. Comparing several silica with e.g. a "1 / Dx(90)" value of approximately 0.3, very different levels of dispersion are received. Therefore, it is not possible to predict the dispersion quality by means of the evaluated analytical parameter. One noticeable result is that all types of silica possessing a "1 / Dx(90)" value higher than 0.5 show a very good dispersion quality. Therefore, it can be assumed that a high value, at least higher than 0.5, gives an indication about the dispersibility of silica.

Discussion

In the following, various aspects are discussed which influence these approaches and show why it is therefore hardly possible to find a suitable correlation respectively prediction. The first compromise which was made during the studies was to adjust the amount of silane to the specific surface area (CTAB) of different types of silica to ensure a consistent level of hydrophobation. However, in this way the viscosity slightly varies from compound to compound which effects the dispersion process. But not adjusting the amount of silane to the surface area would lead on the one hand to an insufficient hydrophobation when using too less silane. On the other hand, a surplus of unreacted silane would decrease the compound viscosity and therefore deteriorate the effective dispersive mixing. Additionally, different surface areas influence the vulcanization system as well, e.g. the higher the surface area is or the higher the porosity is the higher is the possibility that accelerators are adsorbed. Therefore, different obtained dispersion qualities are not exclusively affected by the properties of silica itself.

The types of dosage forms (powders, granules and micro-pearls) in general show a different incorporation behavior. Hence, not adjusting the mixing procedure results in a different effective dispersive mixing time which again affects the final dispersion quality results. Therefore, it is difficult to compare different dosages forms with each other.

The different dispersion measurement methods contain certain limitations as well. The Topography for instance uses filters to limit the minimum and maximum defect area and roughness values which means that the defect area is calculated based on the defects within the height interval of 2 µm to 15 µm. This is due to the fact that bigger particles do not provide reproducible results within the total scanned area of 5 mm² anymore [19]. However, such particles might be present and are not taken into consideration. The evaluation by means of the Dispertester measurement is as well difficult.

There is a certain possibility that different particles being close to each other are not detected as separate clusters but as one big particle due to the two-dimensional evaluation. In addition, a good contrast between particles and rubber is needed to measure the dispersion quality by an optical system. Furthermore, both methods use information about the particle sizes obtained from a freshly cut rubber specimen without knowledge of the full size and shape of different clusters which are partly located underneath the surface.

The rubber compounds consist of roughly 15 different ingredients. Even with a constant mixing procedure and formulation it is hardly possible to achieve precise reproducible in-rubber properties. To show this effect one type of silica (158GR190) was mixed three times, at the beginning, in the middle and at the end of the compound series. Tab. 7 shows the different dispersion qualities measured by means of the Topography and Dispertester for all three batches.

Table 7: Comparison of the dispersion qualities of one compound mixed three times

	batch 1	batch 2	batch 3
Topo: peak area in %	3.4	2.7	4.0
Topo: number of peaks > 2 μm	73	58	56
Dispertester: dispersion in %	89.5	89.0	88.9

Especially in the case of the Topography results, it becomes obvious that the measured dispersion quality varies within the same mixing procedure, which might be due to deviations within the determination and calculation of peaks and peak areas as well. This variation of results increases the difficulties to find a clear correlation to the analytical parameters of silica and therefore restrict a precise prediction of in-rubber properties.

Even though the sedimentation method and in-situ cluster fragmentation provide clear indications to the dispersibility of silica they are limited as well. One major reason is the fact that it is not possible to directly transfer the dispersion process into the laboratory. On the one hand, silica is dispersed inside a high viscous rubber matrix (mixer) including different other ingredients like processing oil which influence the dispersion process. On the other hand, the silica is simply solved inside water in both lab approaches to obtain a suspension which is treated by means of ultrasound. Both processes strongly differ from each other and can therefore not be easily compared.

Summary

In the present paper 25 different types of silica with various analytical parameters and dosage forms were investigated. For these fillers the five standard parameters (CTAB, BET, DOA, moisture content and pH-value) were determined as well as different evaluation parameters obtained by the two new analytical methods: the sedimentation method and the in-situ cluster fragmentation method. All types of silica were mixed in a typical Green Tire formulation with 80 phr of silica (GT80). Two different macro-dispersion measurements systems were investigated to evaluate the dispersion quality, the Topography where the surface roughness of a rubber sample is scanned mechanically by a probe and the Dispertester where the roughness is investigated by an optical light microscopy. Finally, all data were correlated with each other to find the most suitable method to predict the in-rubber dispersibility of silica.

It was shown that the in-rubber dispersion behavior of silica is not dependent on one common single analytical parameter e.g. CTAB or DOA and can therefore not be predicted by a linear correlation. However, by means of two newly developed methods a better indication for the dispersibility of silica can be obtained. The sedimentation method in general shows a linear relation to the Dispertester values with a correlation coefficient of -0.77. However, one type of silica produced by a special process does not fit into the correlation. Therefore, this analytical method is not universally valid for all types of precipitated silica. The in-situ cluster fragmentation demonstrates a pronounced exponential relation instead of a linear correlation. This relation cannot be calculated by means of the Pearson product-moment correlation coefficient r. All types of silica possessing a "1 / Dx(90)" value bigger

than 0.5 show a very good dispersion quality. Therefore, it can be assumed that a high value, at least higher than 0.5, gives an indication about the dispersibility of silica.

Various aspects were discussed which influence these approaches in a sense that it is more difficult to obtain a linear correlation. All these facts lead to the conclusion that the in-rubber dispersibility of silica is influenced by too many factors to be precisely predicted by one analytical parameter. The indications provided by the sedimentation method and in-situ cluster fragmentation are nevertheless a good approach and therefore useful to characterize silica and support the development of new products.

Additional investigations including non-linear approaches are ongoing and moreover combinations of different analytical methods are taken into account. These approaches seem to be very promising in order to get reproducible test results and to get a material specific parameter to predict the in-rubber dispersibility of silica in rubber compounds.

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