Void Volume Measurement - an alternative Approach to Determine the Initial Structure of Silica

Introduction
Since the introduction of the “Green-Tire” by Michelin in 1992 [1], precipitated silica in combination with bi-functional organosilanes became 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, it is still challenging to reach an acceptable level of the abrasion resistance as well. Therefore, highly dispersible silica was developed to attain an equivalent abrasion resistance in comparison to carbon black (CB) filled systems [2].

The basic requirement for the good reinforcing behavior and improvement of different in-rubber properties, especially the abrasion resistance, is a homogeneous compound. Therefore, a good dispersion and distribution of the silica in the rubber matrix is a key factor for success. Dispersion describes the “degree of uniform distribution of a filler’s primary unit (i.e., aggregate of carbon black) into a compound” [3].

To develop new highly dispersible silica it is crucial to be aware of the typical analytical silica parameters and their impact on the dispersion process. One common approach known from the literature is that the structure of fillers affects the in-rubber incorporation and dispersion process substantially [4]. Therefore, the present work focuses on the characterization and measurement of this analytical parameter. The initial structure of silica is usually determined by the DOA measurement whereby dioctyladipate (DOA) is absorbed by the void volume of a filler [5]. This is based on the assumption that a higher void volume indicates a higher initial structure and as a consequence a better dispersion behavior [6]. The DOA method is derived from the OAN (oil absorption number) which was developed for the investigation of carbon black [7]. The DOA number is influenced by the dosage form and the moisture content of a silica sample. Furthermore, this measurement system is limited by the degradation of the chamber and rotors over a period of time [8]. Additionally, working with oil is undesirable due to health issues, the time-consuming measurement and the cleaning process. To overcome these inconveniences an alternative method has to be taken into consideration.

In contrast to silica, there are different methods established to measure the structure of CB. The most common technique is the determination of the OAN which was described above. To get more information about the stability of the CB structure the OAN was evolved into the COAN (compressed oil absorption number) where CB is pre-treated (compressed) before the actual measurement starts [9]. But there is no advantage in the measurement procedure itself, oil is still used. Due to the required extra step, the additional pre-treatment, this method is even more time-consuming. Additionally, silica cannot be investigated with this method due to the fact that the pre-treatment (compression) is not realizable [8]. A further development of the COAN is the calculation of the void volume of CB during a compression and decompression treatment inside a piston/cylinder system [10]. Previous works show a linear correlation between the

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residual void volume of the decompression curve and the structure of CB (Fig. 1) [11]. The residual volume corresponds to the void volume value at atmospheric pressure after decompression, which will be explained in more detail later in this paper.

In the present work, silica was investigated with the above described void volume measurement system. Silica samples with different DOA numbers as well as different dosage forms (powders and granules) were tested. Characteristic values of the curve progression were evaluated and correlated to the DOA measurements.

Experimental part

DOA measurement

The structure of the silica was determined by an Absorptometer „C“ (Brabender® GmbH & Co. KG) in accordance to international standards [5]. The system consists of a mixing chamber and a burette. The void volume of silica (space in between the solid particles) was filled with dioctyladipate (DOA) during the measurement. The silica sample (12.5 g) was mixed with a rotor speed of 125 min⁻¹ inside the kneader while DOA was added with a constant rate of 4 ml / min. During the measurement the torque was recorded permanently. As known from literature [5] this torque is usually low at the beginning, increases rapidly at the point of maximum oil absorption and finally reaches a maximum where the viscosity of the suspension drops again due to the additional oil which can’t be absorbed by the filler anymore (Fig. 2). A polynomial function was calculated out of the raw data. The value for 70% of the polynomial maximum torque was used to finally evaluate the DOA absorption number in ml / 100 g [5].

In accordance to international standards [5] the measurement evaluation is dependent on the silica dosage form. For measuring powder material the moisture content has to be taken into consideration and the DOA absorption number of the dried material has to be calculated. Granules have to be sieved beforehand and a size fraction (1.0 – 3.15 mm) has to be tested [5]. The moisture content was corrected similarly to the powder material.

Compressed void volume measurement

The void volume measurement system (Compressed Volume Structure Tester by HITEC Luxembourg S.A.) consists of a cylinder, a piston (25.4 mm diameter) and a cover (Fig. 3). The piston and the cover include pressure sensors to report the applied and transmitted pressure during a measurement cycle (ca. 3 min measuring time). Additionally, the piston height (sample chamber height) was captured. 2.0 g of a filler sample were compressed with a default pressure rate of 2 MPa / s up to a target pressure of 125 MPa. Subsequently, the pressure was decreased with a constant rate of 2 MPa / s to atmospheric pressure. To avoid additional influences on the final result due to different moisture contents all samples were pre-dried for 2 h at 105°C [10,11]. For granules a size fraction of > 500 µm was prepared by means of a sieve with a mesh width of 0.5 mm.

With a known density ρ in g / cm³ (silica = 2.0 [8] / carbon black = 1.8 [13]) and weight m in g of the silica sample the theoretical volume VT in cm³ can be calculated by equation 1 [10]:

\[ V_T = \frac{m}{\rho} \]  

(eq. 1)

VT represents the absolute volume of the silica without any trapped air and pores. With a known cylinder diameter D in cm and height of the sample chamber h in cm the apparent compressed volume VA in cm³ can be calculated for each single pressure value by equation 2 [10]:

\[ V_A = h \cdot \pi \cdot \frac{D^2}{4} \]  

(eq. 2)

VA represents the total volume of the silica including trapped air due to the filler pores. The difference between the measured apparent volume VA and the theoretical volume VT results in the void volume VV which occurs trapped air inside the sample. The void volume (VV) was calculated per 100 g sample weight (m) in cm³ / g using equation 3 [10]:

\[ V_V = \frac{(V_A - V_T)}{m} \]  

(eq. 3)

Fig. 4 depicts a typical carbon black void volume curve progression evaluated in accordance to international standards [10]. The void volume was calculated for
each single pressure value of the compression and decompression phase. The area between both curves corresponds to the dissipated energy (work) during the measurement. The carbon black sample expands while decompressing and stabilizes finally when atmospheric pressure is reached. The point where the curve hits the y-axis for the first time is determined as the residual void volume.

Results and discussions

Carbon black investigations

In order to obtain a reference for the silica samples, three different types of CB (N326 / N330 / N339) were examined using void volume measurements [9]. A series of samples with different structures (OAN and COAN) and slightly varying external surface areas (STSA [14]) were chosen (Tab. 1).

Fig. 5 depicts the void volume measurements of N326, N330 and N339. Every measurement was repeated three times. The curve progressions of the repeated measurements run precisely on top of each other. The types of carbon black differ in their void volume at every pressure value which can be seen especially at the maximum value of 125 MPa. The higher the measured structure (OAN and COAN) the higher are the calculated residual void volumes.

To confirm what was shown in Fig. 1 [11] a comparison of the COAN and the residual void volumes of the three measured CBs was conducted. Fig. 6 confirms a linear correlation with a coefficient of determination R² of 0,99.

As a first result the void volume measurement can be judged as a suitable method to describe the structure of carbon black. It is able to distinguish between different types of CB and has an appropriate repeatability. The correlation between the COAN structure and the residual void volume measurements known from literature [11] is valid for the three tested CB samples as well. In the next step it was tested if this method can be transferred to silica.

Silica investigations

A variety of silica samples were investigated with the void volume measurement system. Firstly, the repeatability was tested. Fig. 7 depicts the void volume curve for one type of silica measured five times. Similar to carbon black, all measurements run on top of each other. Hardly any expanding (decompression) could be recognized which means that silica remains in the compressed state. This behavior can be explained by the high surface polarity (silanol groups) of silica. While being compressed these silanol groups are forming additional strong hydrogen-bonds which inhibit the decompression. At a certain point, the silica sample gets stuck at one side of the sample chamber whereas it is released from the other side. As a consequence the void volume rises without reaching atmospheric pressure.

Secondly, different types of silica and dosage forms were investigated in order to evaluate their influence on the measurement (Tab. 2). Fig. 8 shows two different silica granules and one silica powder. The curves only differ during the

![Fig. 4: Typical carbon black void volume curve.](image)

![Fig. 5: Void volume measurements of three different carbon blacks.](image)

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compression phase up to 50 MPa. Therefore, it is not possible to evaluate the residual void volume of silica in accordance to the CB void volume method. This same end value is known from in-rubber tests while measuring the Payne-effect (strain sweep) of different types of silica in an identical rubber compound without use of silane. These Payne-effect curves converge at one end value. The final in-rubber structure of silica has to be build-up during vulcanization with the use of bi-functional silanes.

Reproducibility & correlation between void volume and DOA (silica)
The measured void volume curves demonstrate that the residual void volume of silica cannot be evaluated in the same way as for carbon black. However, it is possible to evaluate and distinguish silica curves by considering void volume values at specific pressures (1 to 50 MPa) during the compression phase. For this reason, 16 different silica (powders and granules) with a wide variety of DOA values as well as other analytical parameters (e.g., BET, CTAB, pH value) were examined. Three different operators tested each silica at least four times (minimum twelve measurements). It was found that the best repeatability, reproducibility and distinguishability of different types of silica are given for void volume values at 5 MPa compression pressure. Based on this, the standard deviation was determined (Fig. 9).

The correlation coefficients of the DOA numbers and void volume values at 5 MPa (compression curve) were calculated. Thereby a correlation coefficient of 0.97 can be achieved (Fig. 10).

Comparison of the DOA and void volume method
When comparing both methods the void volume measurement shows clear benefits over the DOA measurement mainly with regard to the measurement time (Table 3). Additionally, the use of oil can be avoided for this measurement process as well as a long undesirable cleaning step. The absence of additionally required chemicals like oil leads to a very clean method without the risk of any health issues. The evaluation of the void volume measurement curves is more precise than the DOA curve evaluation and shows a high repeatability. For the DOA method the moisture content has to be considered whereas for the void volume measurement the silica samples have to be pre-dried. A further long-term study is required to determine possible influences due to the degradation of the piston and cylinder.

Conclusion and outlook
This work presents a new measurement system to determine the initial structure of silica. The void volume method is a favorable alternative to the common DOA measurement due to the fact that it performs faster and avoids the use of oil. The void volume measurements show a proper repeatability and a good differentiation between different types of silica.

Fig. 6: Correlation of COAN vs. residual void volume of CB.

Fig. 7: Void volume measurement of one type of silica measured five times.

Fig. 8: Void volume curves of different types of silica.

Fig. 9: Standard deviation of the void volume values of 16 different types of silica at 5 MPa.
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[8] Internal information, Evonik Resource Efficiency GmbH.
[12] Courtesy of HITEC Luxembourg S.A.

13th Fall Rubber Colloquium – KHK 2018

KHK/DIK The 13th Fall Rubber Colloquium will take place from 6th to 8th of November, 2018 in Hannover (Germany). It is the 13th conference in rubber technology every two years in this series. The previous conferences were highly successful and attracted delegates from a variety of disciplines from around the world. Delegates are encouraged to register both from outside and within Germany. The conference highlights the latest and most important scientific concepts and advanced processing techniques in rubber and polymer science and technology. Experts from all over the world will give keynote presentations. Recognized industrial experts will identify future trends in the rubber industry. Basic researchers will present studies to understand, and therefore, predict the properties of final products. The poster session is an additional good opportunity for scientific discussions and knowledge exchange.

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