Surface properties of non-black fillers

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Abstract. This work was focused on characterization of surface properties of various types of silica used for elastomers. The influence of temperature and length of degassing on the resulting specific surface of silica was studied. Eight types of precipitated and pyrogenic silica samples were investigated in terms of surface characteristics as specific surface, porosity and morphology that directly affects these properties. For characterization was performed using sorption methods, scanning electron microscopy and IR spectroscopy. From the results of the analyzes it was found that the properties of precipitated and pyrogenic silica differ significantly in terms of particle size, structure, porosity and size of specific surfaces. The degassing temperature and time largely influence the behavior of nitrogen adsorption and hence the measurement results.

1. Introduction

In the rubber industry, fillers are used to improve properties or reduce costs. The most common are carbon black and silica [1]. Silica can be used as a promising substitute for conventional carbon black, which, among other things, greatly reduces the rolling resistance of the vulcanizates, thereby reducing the amount of energy consumed and improving fuel efficiency under dynamic load [2]. In the past, white fillers have been used predominantly to achieve the white color of rubber products and reduce their cost. The production and development of synthetic rubbers has made it necessary to solve the problem of light fillers with reinforcing properties. They are mainly used to improve properties such as tensile strength, abrasion resistance, specific gravity and rolling resistance. A number of silanol groups on the silica surface cause high polarity of silica, which always results in poor dispersion in the non-polar rubber and poorer interfacial adhesion between the rubber matrix and the silica. Despite the simplicity of silicates as binary ionic solids and their practical utility, relatively little is known about their surface. In fact, surface properties are highly dependent on the synthesis method and chemical environment, due to the strong reactivity of the silicon oxides and their composition [3]. Synthetic amorphous silica can be divided into two groups according to whether the manufacturing process is by the wet route (precipitated silica) or the thermal route (pyrogenic silica). Since its first production in the early forties of this century, pyrogenic silica has found widespread use in industrial applications. Today, the most important production process is pyrogenic hydrolysis. Pyrogenic hydrolysis consists in the hydrolysis of flame burned silica chloride vapors, whereby cohesive forces produce aggregates and agglomerates of primary silica particles. In terms of morphology, the pyrogenic process provides very fine particles, mostly spherical in shape. Pyrogenic silica is an irreplaceable raw material for many industries. One of the most common applications is the use in paint production, where it is used to adjust the rheological properties. Precipitated silica is a synthetic, fine, white, non-porous form of silica. The basic raw materials for the production of precipitated silica are an aqueous solution of
silicate and an alkali metal such as water glass and acid. The oldest and still the most used application has found precipitated silica as a filler in the rubber industry. This filler can be found in several products, such as soles, steel rope sheathing, technical rubber products and of course tires. By using a precipitated silica mixture with natural or synthetic rubber, some mechanical properties of the vulcanizates can be significantly improved.

1.1. Surface characteristics

The specific surface, or even the specific surface, is determined by the sum of the external surface of the particles and the internal surface of the pores per unit weight. Porosity is defined by the total pore volume per unit weight. By the term pore we can imagine any surface defect of a solid particle in the form of a cavity leading to some extent below the surface of the substance. In general, pores are characterized by shape and size. Due to their geometry, the pore shapes have been generalized to cylindrical, i.e., pores with a circular cross-section and so-called slit pores. We often encounter the occurrence of so-called interparticle spaces formed between solid particles in agglomerates. This phenomenon in analyzes may mimic the presence of meso- to macropores. By the pore distribution we understand the dependence of the volume or surface of the pores on their dimensions. The pore distribution and the shape of the distribution curve depend on their shape [4]. The analytical method used to determine the specific surface area of porous and non-porous solids is known as the BET theory. The use of the method is also described by the International Standard [5] designed to standardize the measurement of specific surfaces by physisorption and also to evaluate BET isotherms [6, 7]. The basis of the theory is the extension of Langmuir's isotherm by further assumptions [7, 8]: the molecules absorb to the solid in layers, there are no interactions between the adsorption layers, Langmuir theory can be applied to each adsorbed layer until the first gas liquefaction occurs.

The present study aims to experimentally explore the structural properties of nanoparticles of different sizes by SEM and IR spectroscopy in order to improve their characterization, the understanding of the structures of the core and of the surface shell.

2. Experimental part

2.1. Materials

To demonstrate the possibilities of the advanced technique, eight commercial samples of pyrogenic and precipitated silica were analyzed. Their main properties are shown in table 1.

| Sample | Process   | Specific surface area (m² g⁻¹) | pH |
|--------|-----------|-------------------------------|----|
| 1      | precipitated | 190 ± 25              | 7  |
| 2      | precipitated | 150 ± 25              | 7  |
| 3      | precipitated | 160 ± 25              | 6.5| |
| 4      | pyrogenic   | 120 ± 25              | 4.1| |
| 5      | pyrogenic   | 300 ± 50              | 4.1| |
| 6      | pyrogenic   | 225 ± 25              | 4.1| |
| 7      | pyrogenic   | 120 ± 25              | 4.3| |
| 8      | precipitated | 180 ± 50              | 6.3| |

2.2. Methods

Before performing the nitrogen sorption and porosimetry measurements, the silica samples were degassed for 16 hours under primary vacuum at 6.66 Pa and 160 °C.
Conventional techniques
The Quantachrome Nova 1200e was used to analyze the surface properties of silica. All samples were studied by physical nitrogen adsorption at liquid nitrogen temperature, under vacuum. The measured values were processed in the NovaWin2 program to a multipoint BET isotherm ($S_{BET}$ specific surface area), t-line (pore volume and surface area), and pore distribution using the BJH method from the desorption part of the isotherm. The device is equipped with two stations. One is for analysis and the other is used to treat samples by degassing. In a degassing station, two samples can be degassed simultaneously. The exact degassing temperature is provided by two separate heating elements equipped with a thermostat.

Advanced technique
The particle sizes, agglomerates and interparticle spaces of the investigated silica samples were analyzed using the TESCAN VEGA3 Scanning Electron Microscope. All images are taken in secondary electron mode and provide micro-views of the surface of the samples to be examined. Measurements of particle sizes and interparticle spaces of individual samples were made using the program. The prepared samples were plated with a fine layer of Au-Pd and placed in a microscope chamber.

ATR measurements
The samples of silica were characterized by ATR spectra obtained on a NICOLET iS 50 spectrophotometer Thermo Scientific, with resolution of 4 cm$^{-1}$. After inserting the sample into the instrument, a diamond crystal was pressed onto the sample surface to measure ATR spectra.

3. Results and discussion

3.1. Conventional techniques
Using the BET method, the specific surface area $S_{BET}$ of the aggregates can be determined. The specific surface area is of interest in this context as it allows conclusions to be drawn about the size of the primary particles.

Sample 1 is silicon dioxide conventionally used in rubber production. It is available in powder form, and the individual particles are spherical in shape. The specific surface area $S_{BET}$ is 188.57 m$^2$ g$^{-1}$, with a $C_{BET}$ value of 174.9, we can see in table 2. The presence of micropores confirms the processing of sorption data into the t-line, where the surface of micropores $S_{mikro}$ = 28.59 m$^2$ g$^{-1}$ and external surface $S_{ext}$ = 144.112 m$^2$ g$^{-1}$. The resulting specific surface area of the t-line $S_t$ = 188.568 m$^2$ g$^{-1}$. It can be seen from the BJH sorption data that sample 1 is predominantly mesoporous. Most pores range in diameters from 4 to 17 nm. The 9 nm pore diameter is the most widely distributed, with the result of the analysis showing the exact result of 9.08 nm.

| Sample | $S_{BET}$ (m$^2$ g$^{-1}$) | $C_{BET}$ (-) | $S_{ext}$ (m$^2$ g$^{-1}$) | $S_{mikro}$ (m$^2$ g$^{-1}$) | $d_{por}$ (nm) | $d_{agl}$ (µm) | $d_{prim}$ (nm) | $d_{mp}$ (nm) |
|--------|--------------------------|--------------|---------------------------|-----------------------------|---------------|---------------|----------------|-------------|
| 1      | 188.57                   | 174.9        | 144.112                   | 28.59                       | 9.08          | 174.21        | 100            | 200         |
| 2      | 146.63                   | 373.7        | 115.123                   | 23.409                      | 24.59         | < 240         | 100            | 70          |
| 3      | 163.84                   | 293.5        | 122.965                   | 40.875                      | 6             | 10.02         | 38.16          | 65.6        |
| 4      | 127.39                   | 16.5         | 122.573                   | 0                           | 3.41          | 27.33         | -              | -           |
| 5      | 281.9                    | 160.5        | 225.786                   | 56.113                      | 3.42          | 1.92          | 63.8           | 135.1       |
| 6      | 182.93                   | 147.4        | 151.925                   | 31.004                      | 3.41          | 1.1           | 37.22          | 83.73       |
| 7      | 120.48                   | 46           | 117.148                   | 3.33                        | 3.41          | 1.88          | 35.79          | 108.31      |
| 8      | 182.36                   | 396.2        | 144.112                   | 28.59                       | 18.87         | 11.23         | 35.85          | 52.13       |
As in the previous silica sample 1, sample 2 is a commonly used, precipitated silica in the rubber industry. It is used to improve tire properties such as abrasion resistance and road grip. It is also supplied in the form of micropellets of predominantly spherical shape. By software interpretation of the results from the t-line we obtained satisfactory values of specific surface $S_t = 146.63 \, \text{m}^2 \, \text{g}^{-1}$, of which the total surface of $S_{\text{mikro}}$ micropores is $23.409 \, \text{m}^2 \, \text{g}^{-1}$ (table 2). The BJH method was used to determine the pore distribution in sample 2 with a total pore surface of $115.123 \, \text{m}^2 \, \text{g}^{-1}$.

Sample 3 is a white, synthetic, amorphous silica with a wide range of uses in various rubber products. An increased $C_{\text{BET}}$ value of 293.5 may again be related to the presence of micropores in sample 3. The specific surface area $S_{\text{BET}} = 163.84 \, \text{m}^2 \, \text{g}^{-1}$ was determined by the BET method. The t-line sorption data processing yielded $S_{\text{mikro}} = 40.875 \, \text{m}^2 \, \text{g}^{-1}$ and $S_{\text{ext}} = 122.965 \, \text{m}^2 \, \text{g}^{-1}$. By summing the resulting specific surfaces from the t-line method, we obtained the resulting specific surface $S_t$, which coincides with the BET isotherm. The pore distribution from desorption part of the isotherm by the BJH method shows a maximum at a diameter of about 6 nm. A pore distribution of up to 20 nm in diameter can be observed on the curve. The sample 3 can therefore be characterized as predominantly mesoporous.

Sample 4 is a pyrogenic silica, used predominantly as an additive in epoxy adhesives and coatings, to ensure that the mixture is thickened and prevents pigment deposition. When evaluating the BET isotherm, the $S_{\text{BET}}$ value is $127.39 \, \text{m}^2 \, \text{g}^{-1}$ at $C_{\text{BET}} = 16.5$. The $C_{\text{BET}}$ value of sample 4 is unusually low and therefore a comparison of the specific surfaces of the BET isotherm and the t-line method is necessary. Processing of the sorption data into the t-line resulted in a $S_{\text{ext}} = 122.573 \, \text{m}^2 \, \text{g}^{-1}$, with no microporosity. The resulting difference between $S_{\text{BET}}$ and $S_{\text{ext}}$ could be due to a measurement error. One possible error could be an abnormality in the BET isotherm in the range of relative pressures of 0.8 to 1.2.

Sample 5 is a synthetic pyrogenic silica commonly used in the manufacture of inks, gel coatings. It is also used as an additive modifying the rheological properties of adhesives and paints. From BET isotherm the value $S_{\text{BET}}$ is $281.9 \, \text{m}^2 \, \text{g}^{-1}$ at a $C_{\text{BET}}$ value of 160.5. This value is close to the upper limit of validity for samples with mesoporous character. The t-line method found $S_{\text{ext}} = 225.786 \, \text{m}^2 \, \text{g}^{-1}$ and $S_{\text{mikro}} = 56.113 \, \text{m}^2 \, \text{g}^{-1}$. The sum of the external surface and the total micropore surface corresponds to the value measured by the BET method. The total micropore volume in the sample 5 according to the t-line is 19.9%.

Sample 6 is a synthetic pyrogenic silica with a wide range of uses, such as e.g. personal hygiene products, epoxy and polyurethane fillers or gel batteries. The characteristics do not differ much from sample 5. The BET method measured $S_{\text{BET}}$ values = $182.93 \, \text{m}^2 \, \text{g}^{-1}$ and $C_{\text{BET}}$ constant is 147.4. The constant value corresponds to the characteristic range for mesoporous substances. The total content of $S_{\text{mikro}}$ micropores according to the t-line corresponds to 31.004 m$^2$ g$^{-1}$. The resulting external surface $S_{\text{ext}} = 151.952 \, \text{m}^2 \, \text{g}^{-1}$. The sum of these surfaces coincides with the specific surface area determined by the BET method. Using the BJH method, the pore distribution of sample 6 was obtained from the desorption branch. It is almost no different from sample 5. It reaches the maximum at a pore diameter of 3.41 nm.

Sample 7 was the last of the characterized pyrogenic silica. Like samples 5 and 6, it is used in personal care products, in the manufacture of paints and adhesives. $S_{\text{BET}}$ specific surface area is $120.48 \, \text{m}^2 \, \text{g}^{-1}$. The $C_{\text{BET}}$ constant of 46 is at the lower limit characteristic of mesopore materials. Accordingly, as in previous samples, the t-line method must be used. The values obtained by this analysis confirmed a low total micropore content of $S_{\text{mikro}}$ is $3.33 \, \text{m}^2 \, \text{g}^{-1}$.

The last sample 8 is a classic example of precipitated silica used in rubber production. Its biggest use is in the production of tires, cable sheathing and rubber soles. Use in a rubber compound affects the properties of vulcanizates such as tear resistance, Shore hardness, tensile strength and abrasion resistance. The BET isotherm confirms the low incidence of micropores. This was also confirmed by the $C_{\text{BET}}$ Const, which is unusually high for sample 8, up to 396.2. The specific surface area of the BET isotherm was determined to be $182.36 \, \text{m}^2 \, \text{g}^{-1}$. Given the assumed occurrence of micropores, it was necessary to compare the results of the BET method with the t-line method. The total surface area of the micropores determined by the t-line is $28.59 \, \text{m}^2 \, \text{g}^{-1}$ and the external surface is $144.112 \, \text{m}^2 \, \text{g}^{-1}$.
The sum of these values coincides with the resulting specific surface area as determined by the BET method. The BJH method showed a wide pore distribution, with a maximum at 18.87 nm.

3.2. Advanced technique

Electron microscopy can provide an analysis of the aggregate structure with regard to its shape and in particular the number of primary particles per aggregate. Images of the samples using a scanning electron microscope (SEM) are shown in figures 1–16.

As mentioned above, the sample 1 is supplied in the form of microspheres, spherical in shape with a particle size of 140–190 µm (figure 1). A more detailed look at the surface of these particles revealed that the particle structure is formed by agglomerates of primary particles. These primary particles can be recognized already at a magnification of 10000×. For measurement needs and higher accuracy we have chosen a magnification of 25000× (figure 2).

Figure 1. SEM imagine and particle measurement of sample 1 at 200× magnification.

D1–D3 measurements show that the average primary particle size is about 0.1 µm. For sample 1, it was possible to measure the diameters of some larger and well visible interparticle spaces. Accordingly, measurements of D4–D6 have shown that the diameter of the interparticle spaces can reach dimensions above 0.2 µm.

Figure 2. SEM imagine and measurement of primary particles of sample 1 and interparticle spaces at a magnification of 25000×.
Images of sample 2 taken with SEM confirm the assumption of similarity to sample 1. In figure 3 we can see particles of mostly spherical shape with dimensions up to 240 µm. Looking closer at the surface of these particles, we observed a lower incidence of clumps of primary particles. The measurements of the diameter of the primary particles $D_1$–$D_3$ in figure 4, and the mean value $d_{\text{prim}} = 0.1$ µm obtained from them, show similarity to sample 1.

At a magnification of $25000\times$, we were also able to measure the size of interparticle spaces. These can be seen in figure 4, measurement $D_4$–$D_6$. The average value of the measurements is 70 nm.

![Figure 3. SEM imagine of sample 2 particles, measured at 200× magnification.](image)

![Figure 4. SEM imagine and measurement of primary particles of sample 2 and interparticle spaces at a magnification of 25000×.](image)

From SEM images of sample 3, differences in the particle shape of the sample are clearly discernible compared to samples 1 and 2 (figure 5). In contrast, the particles in sample 3 are of significantly different shapes. The primary particles are arranged in aggregates ranging from several µm to several tens of µm. The average silica particle size from measurements $D_1$–$D_3$ in figure 5, is 10.02 µm.

The differences in structure are also evident from the point of view of primary particles, which are characterized by very small dimensions (figure 6).

From measurements $D_1$–$D_3$ in figure 6, the average primary particle size was 38.16 nm. The nature of the sample allowed the observation of primary particles at a magnification of up to $100000\times$. Such a magnification allowed us to take a closer look at the interparticle spaces. The measurements of $D_4$–$D_6$ in figure 6 reveal a diameter of 50.86–76.06 nm. Interparticle spaces with the indicated diameter can imitate meso- to macropores in sorption analyzes.
The morphology assessment of sample 4 by SEM microscopy has shown that the pyrogenic silica sample is predominantly composed of primary particle aggregates of very small dimensions (figure 7). Larger agglomerates were also observed in the sample. D1–D3 measurements showed an...
average size of 27.33 µm. The nature of the sample did not allow us to use a magnification at which primary particles could be observed and measured at the same time. From figure 8, it is apparent that the primary particles have very small dimensions, only a few tens of nm, and form dense network structures.

![Figure 8. SEM imagine of structure of sample 4 at 25000× magnification.](image)

The similarity of samples 4 and 5 is also confirmed by SEM images (figure 7 and 9). Sample 5 consists mainly of small aggregates of primary particles (figure 9), which rarely form larger agglomerates. From measurements D1–D3 in figure 9 at a magnification of 5000×, the average aggregate size was determined to be 1.92 µm.

![Figure 9. SEM imagine and particle measurement of sample 5 at 5000× magnification.](image)

In a 50000× image (figure 10), primary particles and the space between them were observed. The average particle size was 63.8 nm using D1–D3 measurements. D4–D6 measurements represent a selection of interparticle spaces with the largest dimensions, and have an average size of 135.1 nm.

The morphology of sample 6 is very similar to sample 5. SEM images confirmed the presence of small agglomerates with an average size of 1.1 µm (figure 11). Figure 12 provides a more detailed view of the sample structure and the size of the primary particles and interparticle spaces. The average particle size as measured by D1–D3 in figure 12 is 37.22 nm. The diameter of the interparticle spaces from D4–D6 measurements is 83.73 nm.
From a morphological point of view, sample 7 is not very different from samples 5 and 6. It consists of agglomerates of indeterminate shapes with an average size of 1.88 μm (figure 13). Primary particles and
interparticle spaces were observed in a SEM image with a magnification of 100000× (figure 14). The average particle size of 35.79 nm was calculated from the primary particle size measurements D1–D3. The mean value of interparticle space sizes from D4–D6 measurements is 108.31 nm.

Figure 13. SEM imagine and particle measurement of sample 7 at 10000× magnification.

Figure 14. SEM imagine and measurement of primary particles, interparticle spaces of sample 7, at a magnification of 100000×.

Figure 15. SEM imagine and particle measurement of sample 8 at 2000× magnification.
By evaluating the SEM images, we conclude that sample 8 is most morphologically similar to sample 3. It consists of agglomerates of larger sizes. In the image (figure 15) the agglomerates are clearly visible at a magnification of 2000×. Their average size was determined from D1–D3 measurements and reached 11.23 µm.

The primary particles and interparticle spaces are shown in figure 16. The average primary particle size was calculated from D1–D3 measurements and its resulting value was 35.85 nm. The diameter of the interparticle spaces from the measurements corresponds to 52.13 nm.

![Figure 16. SEM imagine and measurement of primary particles, interparticle spaces of sample 8, at a magnification of 80000×.](image)

### 3.3. ATR measurements

The ATR spectra of pyrogenic silica samples (4, 5, 6 and 7) are shown in figure 17. The characteristic bands almost at 1090, 810 and 470 cm\(^{-1}\) correspond to the stretching, bending and out of plane of Si-O bonds, respectively. The position and the shape of the main Si-O vibrational band at 1090 cm\(^{-1}\) shows a stoichiometric silicon dioxide structure.

![Figure 17. The ATR spectra of pyrogenic silica samples.](image)

The ATR spectra of precipitated silica samples (1, 2, 3 and 8) are shown in figure 18. The absorption peaks at 459, 799, 1097, 952 cm\(^{-1}\) correspond to the bending vibration, symmetric stretching vibration, asymmetric stretching vibration of Si-O-Si and bending vibration of Si-OH, respectively [9]. The absorption peak at 1638 cm\(^{-1}\) correspond to bending and stretching vibration of OH.
Figure 18. The ATR spectra of precipitated silica samples.

4. Conclusion
The aim of this paper is to combine results from surface chemistry and particle characterization in order to understand the basic mechanisms of pyrogenic and precipitated silica applications. Recent investigations in the field of surface characterization and interactions are reported. By using modern methods and instrumental analyzes, the specific surfaces, porosity and morphology of eight silica samples were determined. These properties are directly related to the reinforcing properties of silica, the extent of its dispersion, and overall to the properties it affects in the rubber composition. Use of a suitable silica can improve tire abrasion resistance, reduce tire rolling resistance, reduce cost and reduce environmental impact. From an economic and environmental point of view, mineral fillers are a progressive material. Better understanding of their surface properties and subsequent adjustment to specific needs could produce new, higher quality, cheaper and more environmentally friendly rubber products in the future.

5. References
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