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Synthesis of precipitated silica from sodium silicate solution by carbonation method

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ABSTRACT

A method was proposed for the preparation of silica powders using sodium silicate as the silica source and carbon dioxide and hydrochloric acid as precipitating reagents. The effect of reaction temperature (20, 40, 60, and 80 °C) and SiO_2 concentration in sodium silicate solutions (4, 6, 8, and 10 %) on silica morphology, dibutyl phthalate absorption, aggregate size distribution, and dispersion ability (agglomerates fragility) were investigated. The best properties of silica powder were achieved at reaction temperature 40 °C and SiO_2 concentration 8 %. The properties of the silica sample obtained at optimal conditions were compared with properties of high-quality commercial silica used as rubber reinforcing filler. Also, the vulcanization characteristics and mechanical characteristics of rubber composites containing these two silica fillers were investigated. It was found that silica filler with excellent properties can be produced using the proposed method, while by tuning temperature and precursor concentration, the silica properties that are important for its reinforcing potential may be closely controlled.

Keywords: Silica, Sol-gel processes, Scanning electron microscopy (SEM), Light scattering, Rubber reinforcing

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1. Introduction

Shortly after sulfur silanes began to be used as coupling agents, colloidal silica has found extensive application as reinforcing filler in rubber. In the last decades, it widely replaced carbon black, traditional reinforcing filler for tires, owing to its ability to improve the rolling resistance with little or no ~~r~~reducing efficiency in traction or wear [1]. Although the synthesis procedures for colloidal silica and carbon black are drastically distinguished, the resulting structure of particles, aggregates, and agglomerates is surprisingly similar [2]. Silica structure is complex and consists of primary particles, aggregates, and agglomerates (Figure 1). Primary particles are the base structures formed as a result of nucleation and growth. Aggregates are clusters of primary particles characterized by extensive bridging between particles. Agglomerates are softer structural elements and are made up of aggregate~~s~~ clusters [3].

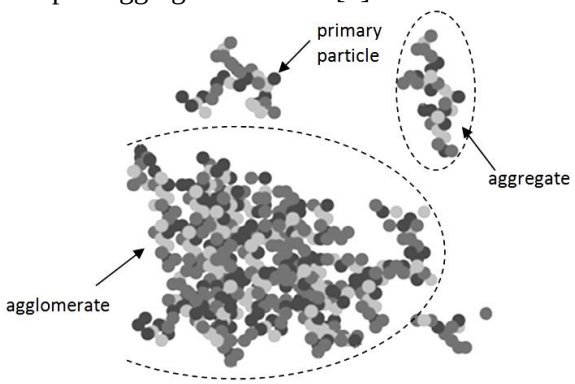

Figure 1. Structural elements of precipitated silica

To be effective when used in elastomeric composite production, the filler must be both highly dispersive and highly reinforcing. These properties are heavily dependent on the filler's structure [4-8]. A number of methods such as chemical vapor deposition, plasma and combustion synthesis, hydrothermal method, and sol-gel processing have been used for the synthesis of the colloidal silica particles [9]. Recently, alternative raw materials such as pumice, rice husk ash, oat husk ash, sugar cane, bagasse ash, and corn cob ash have been used to produce amorphous silica [10, 11]. Nevertheless, the most commonly used method for silica production is the neutralization of sodium silicate solution by a mineral acid (sulfuric, carbonic, or hydrochloric), which belongs to the category of sol-gel processes. Sodium silicate solution is mixed with acid under continuous agitation at elevated temperature. This results in the formation of silicic acid (H_4SiO_4), followed by nucleation, growth, and aggregation of silica particles. This produces a slurry with low solids content containing the amorphous silica and residual salts, either sodium sulfate, sodium chloride, or sodium carbonate. The salts are removed by washing in a counter-current decantation system or by filter press. Drying is the last operation in the production of silica. The type and characteristics of the solution, as well as temperature, pH value, and other factors, have a major effect on the product's structure and properties [7].

Although the majority of researchers used sulfuric and hydrochloric acids for sodium silicate solution neutralization, carbonation methods also have been considered. This approach allows obtaining silica powders at low cost using inexpensive raw materials and to absorb the greenhouse gas of carbon dioxide. Cai et al [12] prepared ultrafine silica powders from the aqueous sodium silicate in a high-pressure reactor under stirring at a certain temperature. Carbon dioxide was injected into the reactor at elevated pressure. Chattopadhyay and Gupta [13] proposed a method for the precipitation of silica nanoparticles using supercritical CO_2. A water-in-oil microemulsion of an aqueous sodium silicate solution in n-heptane or isooctane is injected into supercritical CO_2 which rapidly extracts the solvent from the droplets and reacts with the exposed aqueous sodium silicate reverse micelles, forming silica nanoparticles. The precipitated silica prepared by reaction of sodium silicate and gas CO_2 on the fixed-bed column has also been produced successfully [14]. Even though these techniques allow tailoring of silica properties through strict control of process parameters, they still are relatively complicated and time-consuming. In the present work, the authors proposed a simple and inexpensive carbonation technique to synthesize silica particles. Amorphous silica obtained by this process can be produced in large quantities, at low costs, and by the sustainable method. The method consists of two stages: in the first stage the sodium silicate solutions were bubbled with CO_2/air mixture, and in the second stage, acidification was continued with the addition of hydrochloric acid into the solution until the desired pH value. Effects of SiO_2 concentration in solution and reaction temperature on silica properties were investigated.

2. Experimental

2.1. Silica particles synthesis

The commercial aqueous solution of sodium silicate having modulus (SiO_2/Na_2O molar ratio) 2.8 was used for silica precipitation. Other characteristics of sodium silicate were: specific weight: 1.54 g/cm3, the content of SiO_2 33.25%, and content of Na2O 12.16%. In the initial stage, diluted sodium silicate solutions were carbonated by a mixture of 65 % of air and 35 % CO_2. In the second stage, acidification was continued with the addition of hydrochloric acid (2.0 M) to the solution until the pH value of the solution decreased to 6. Precipitation produced low solid content sediment consisted of hydrated silica and NaCl. Then, the salt was washed out by decantation and filtration. A silver nitrate test was carried out on filtrates to detect the presence of salt. Drying of sediment at 300°C was the final operation, and as a result, the silica powder was obtained. A scheme of the experimental setup is shown in Figure 2, and the protocol for silica precipitation is presented in

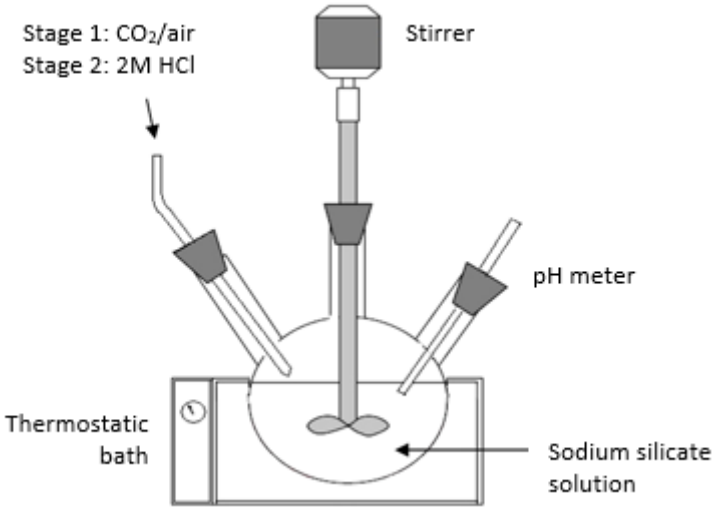

Figure 2. Experimental setup for silica synthesis

Table 1. Silica precipitation protocol

Step No.	Operation	Time
1.	Mixing of distilled water and sodium silicate at constant temperature	30 min
2.	Introduction of CO_2/air mixture in solution (until pH decrease to 9.5-10)	150 min
3.	Ageing of dispersion	30 min
4.	Introduction of diluted HCl in solution (until pH decrease to 6)	60 min
5.	Ageing and correction of pH value	180 min
6.	Decantation, filtration and multiple washing of precipitate	-
7.	Drying	-

2.2. Silica particles characterization

The effects of reaction temperature and SiO_2 concentration in sodium silicate solutions on silica properties were investigated. To evaluate reaction temperature influence samples were prepared from a solution containing 8 % of SiO_2 at 20°C, 40°C, 60°C, and 80°C. To assess the influence of SiO_2 concentration on silica properties, the solutions containing 4 %, 6 %, 8 %, and 10 % SiO2 were prepared, while the reaction temperature was at 40°C. Silica morphology, dibutyl phthalate (DBP) absorption, and dispersion ability were tested on synthesized silica samples. Also, commercial reinforcing filler Ultrasil 7005 was subjected to the same tests to compare it with filler obtained through the carbonation method.

The morphology of precipitated silica was studied by scanning electron microscopy (SEM) on the JEOL-JSM-6460LV microscope operating at 20kV. Prior to SEM imaging, the samples were coated with a thin layer of gold.

The oil absorption of silica was determined by the MA.TS.02 standard technique which is often used in the characterization of powders in industry and gives reproducible results [15, 16]. Dibutyl phthalate (DBP) was added at a rate of 0,2 ml/min to the scoop containing dry powder. Oil and powder were carefully mixed until compacted mass was formed there had no noticeable presence of DBP at scoop surface. The measured DBP volume (per gram of investigated sample) was recorded and expressed as the oil absorption of the investigated powder sample.

Light scattering is applied to assess the dispersing ability of silica [17]. The fragility of the agglomerates is assessed by observation of agglomerate disruption after exposure to intense ultrasound. Dispersing ability of filler is inversely proportional to the strength of agglomerates [2, 17]. The dispersion in aqueous suspensions

of silica samples was investigated by using the Malvern Mastersizer 2000 instrument. In all the experiments, the silica samples were dispersed in water, and the effect of sonication on the breakup of agglomerates was investigated through recording of the percentage of incident light blocked by suspended particles (obscuration) that increase after each sonication cycle. The dry powders were added to the circulation bath until the obscuration reached 5-6 %. The obscuration increased after each run due to a progressive break up of agglomerates with increasing the sonication time. The greater the increase in obscuration, the softer the agglomerates, and the better the filler dispersing ability. The stirrer was maintained at 1200 rpm and the sonication time for each cycle was fixed at 20 seconds. The sonication power was maintained at 100 % during all tests.

2.3. Preparation of rubber compounds

The formulation of rubber compounds is listed in Table 2. Natural rubber of a grade SMR10cv was the matrix in this study. A selected sample of the synthesized silica and commercial silica Ultrasil 7005 by Evonik were used as reinforcing filler. Silane Si 69® (Bis [3-(triethoxysilyl) propyl] tetrasulfide) obtained by Evonik was used as a coupling agent. Binary acceleration system N-Cyclohexylbenzothiazole-2-Sulfenamide (CBS) and diphenyl guanidine (DPG) has been selected for the study. Also, ZnO, stearic acid, aromatic oil, and sulfur were used as additives.

Table 2. Formulation of rubber compounds

Ingredient	SMR10cv	Silica	Stearic acid	ZnO	Silane Si69	Aromatic oil	Sulphur	CBS	DPG
Phr[1]	100	50	2.0	2.5	3.0	4.4	1.7	1.7	2.0

Mixing of rubber compounds was carried out in a laboratory mill with two rolls of dimensions 400× 160 mm, at a speed ratio of the rollersn_1/n_2= 28/22, and at a roller temperature of 30–40°C.

2.4. Characterization of rubber compounds

The cure characteristics were assessed by a Monsanto oscillating disc rheometer R-100, according to the ASTM D2084-95 standard testing method. The optimum curing time (t_{90}) was determined at 160°C. Cure characteristics of rubber compounds were determined by oscillating disc rheometer (ODR) in accordance to ASTM D 2084-01. Torque parameters: min. torque (M_L), max. torque (M_H), torque difference (M_H-M_L), and cure parameters: scorch time (ts_1,ts_2), vulcanization time (t_{10}, t_{30}, t_{50}, t_{60}, t_{90}), and curing rate index (CRI) were obtained in these tests. Rubber samples for mechanical tests were prepared according to ASTM D 3184-80 and conditioned according to ASTM D832-07. Abrasion Resistance (ASTM D5963), shore hardness (*ASTM* D2240), and the tensile properties: tensile strength, modulus and elongation (ASTM D412) of the silica filled rubber samples were determined.

3. Results and discussion

3.1. Precipitated silica properties

3.1.1. Morphological properties

SEM images of the samples obtained at reaction temperatures 20°C, 40°C, 60°C, and 80°C under the same all other process conditions are shown in Figure 2 and SEM images of the samples obtained from solutions with

[1]Parts per hundred rubber

4%, 6%, 8%, and 10% SiO_2 are shown in Figure3. To better distinguish differences between silica structures, micrographs were taken at three different magnification levels: 300×, 3000× and 30000×. A simple visual comparative analysis of micrographs shown in Figure 3 and Figure 4 reveals clearly that both reaction temperature and SiO_2 concentration in solution significantly affect silica morphology. The micrographs taken at magnification levels 300× and 3000× show whether agglomerates are dense or porous, while at magnification 30000× primary particles can be observed. From the micrographs shown in Figure 3 it can be seen that silica obtained at 20°C consists of dense, compact agglomerates while agglomerates of silicas obtained at higher temperatures are porous and loose.

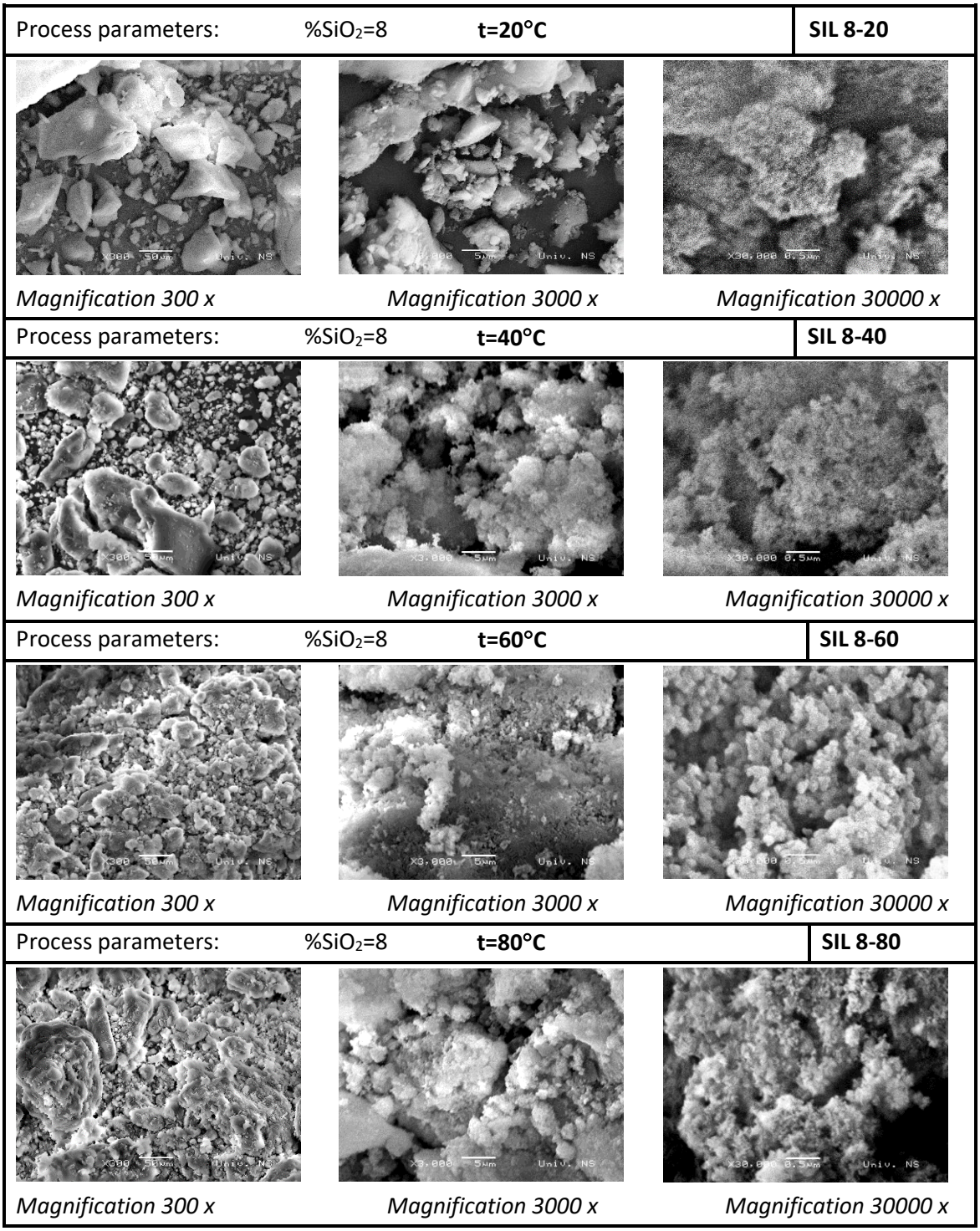

Figure 3. The effect of reaction temperature on silica morphology

SEM images taken at magnification 30.000× show that the largest primary particles were obtained at 60°C. The micrographs shown in Figure 4 reveal that solution containing 4 % yield dense agglomerates, while more porous agglomerates are produced when SiO_2 concentration was 6 %, 8 % and 10 %.

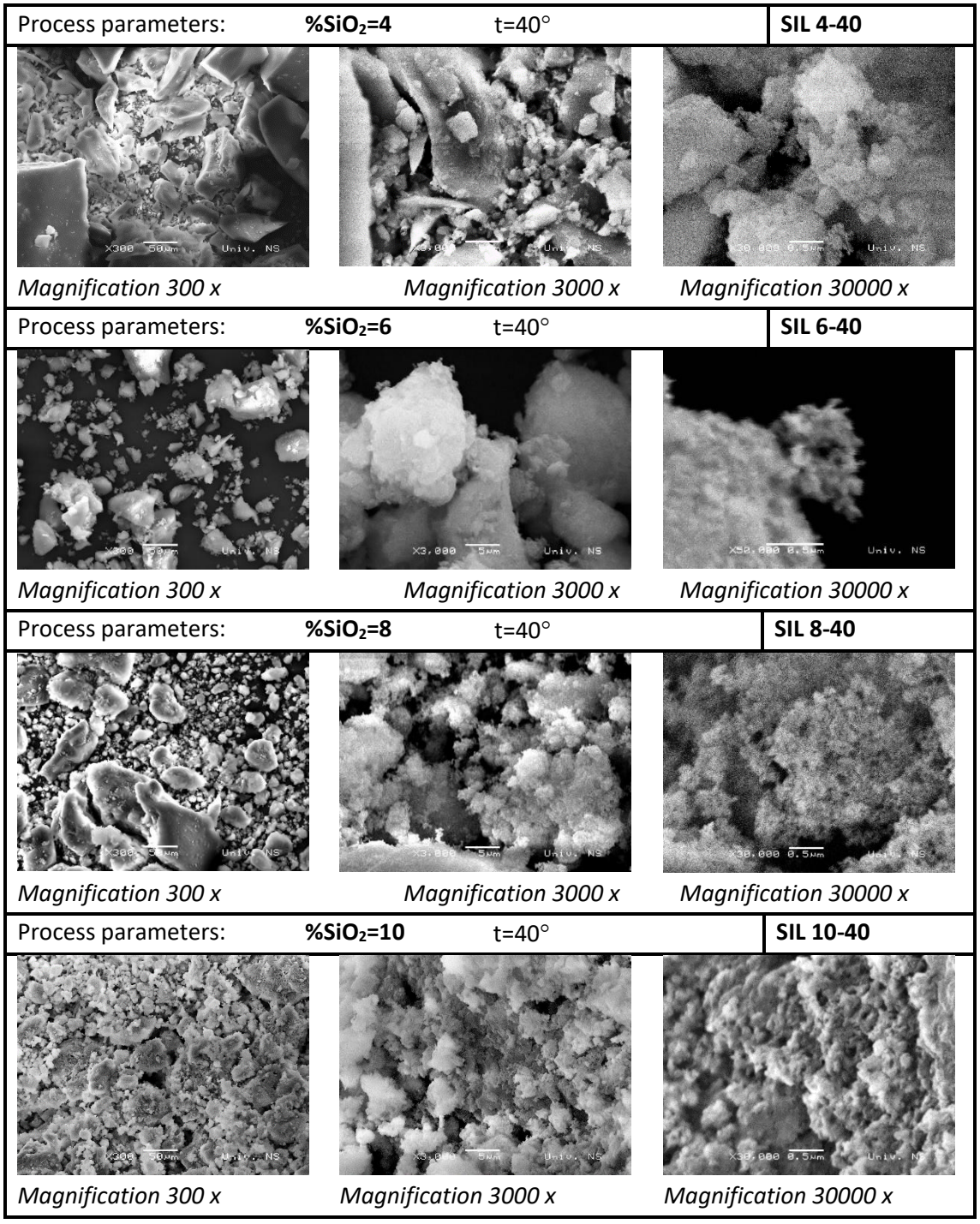

Figure 4. The effect of SiO_2 concentration on silica morphology

3.1.2. Dispersion in aqueous solution

The test results of silica dispersion ability in an aqueous solution are shown in Figure 5. Figure 5.a shows that silicas synthesized from solutions at 20°C and 80°C are not responsive to sonication, which indicates that they consist of hard agglomerates. A significant increase in obscuration after each sonication run was recorded in silicas obtained at 40°C and 60 °C. Figure5.b shows that silica obtained from a solution containing 4 % SiO_2

also resist sonication. Silica obtained from a solution containing 8 % SiO_2 at 40 °C is the most responsive to sonication, so it can be concluded that these process parameters give a product with the highest dispersing ability.

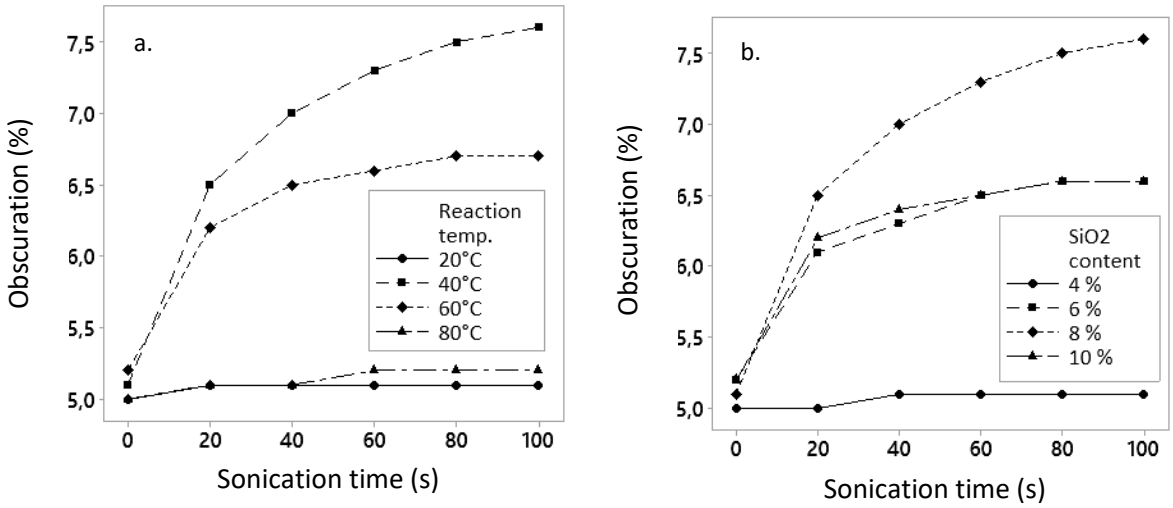

Figure 5. Effect of sonication time on silica deagglomeration

3.1.3. DBP absorption

The results of DBP absorption testing of silica samples are given in Figure 6. The effect of reaction temperature at constant SiO_2 concentration (8%) is shown in Figure 6.a. The maximal value of DBP absorption is obtained at 40°C. Figure 6.b shows that SiO_2 concentration significantly influenced DBP absorption of silica. At the temperature of 40°C, the highest value of DBP absorption was measured on the samples obtained from solutions contained 8 % of SiO_2. These results are consistent with morphological characteristics of silica powders determined by SEM analysis.

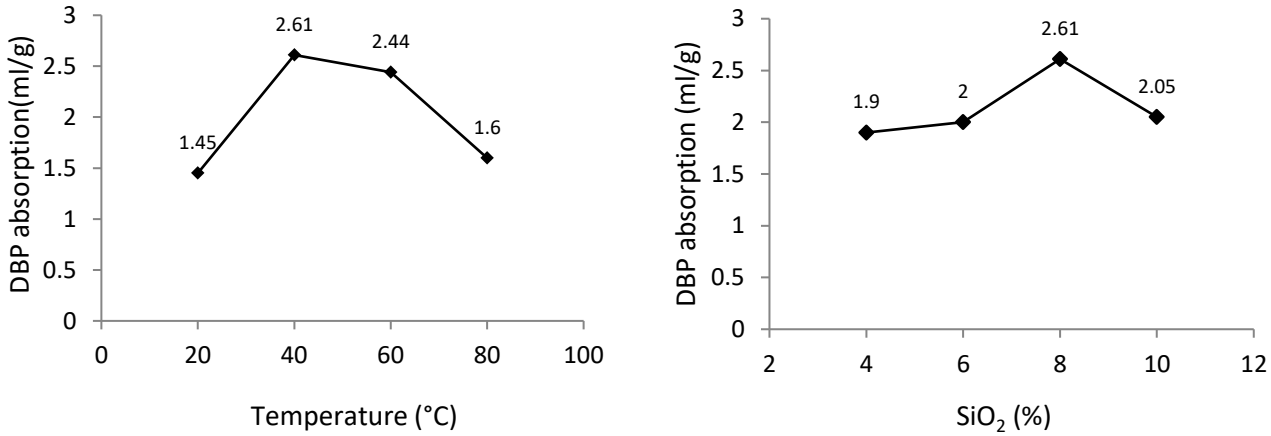

Figure 6. DBP absorption of silica samples dependence on reaction temperature (a), and SiO_2 concentration (b)

3.1.4. Aggregate size distribution

Charts displayed in Figure 7 illustrate the effect of reaction temperature (a, b, c, d) and SiO_2 concentration (e, f, g, h) on aggregate size distribution. From Figure 7 (a-d) it can be seen that at 20°C precipitation reaction yields silica with the greatest median diameter (d(0,5) = 26,1) μm and broader particle size distribution that tend to be bimodal. An increase in temperature to 60°C results

in decreasing of d(0,5) and narrowing aggregate size distribution, while the slight increase of fraction -2,0 μm was recorded in silica obtained at 80°C. Charts e-h show that increasing SiO_2 concentration results in narrowing aggregate size distribution.

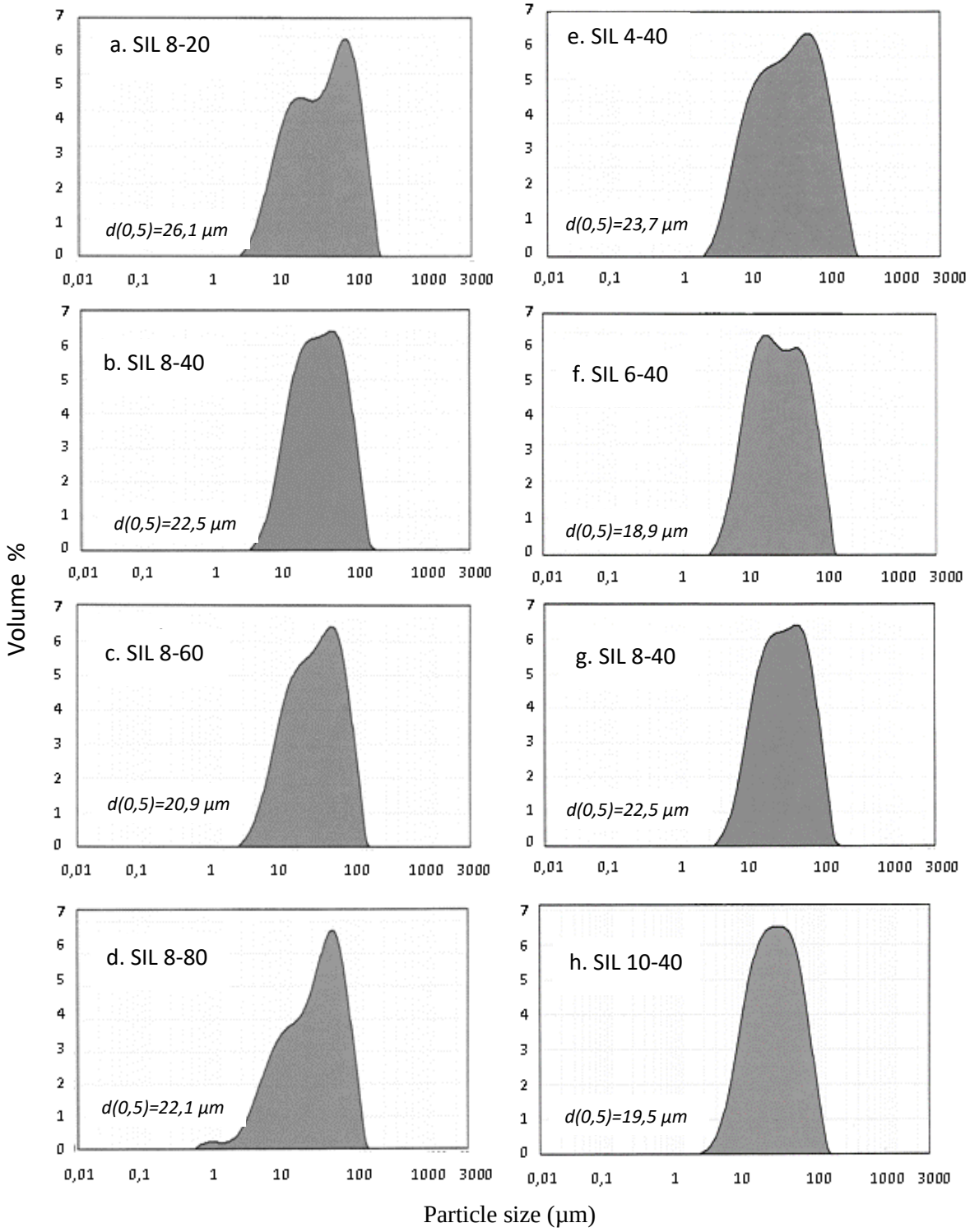

Figure 7. Aggregate size distribution of silica dependence on reaction temperature and SiO_2 concentration

3.1.5. Comparison of Ultrasil 7005 and silica obtained by carbonation method properties

The assumption that highly effective rubber reinforcing filler can be produced by the proposed carbonation method was confirmed by comparing morphology characteristics, DBP absorption, aggregate size distribution, and dispersing ability of selected synthesized silica sample and the sample of highly dispersible silica Ultrasil 7005 by Evonik, widely used as reinforcing filler in the rubber industry. To estimate the quality of the produced precipitated silica, the sample with the best characteristics SIL 8-40, which has the highest DBP absorption and the best dispersion ability of all synthesized fillers, was compared with commercial filler, highly dispersible silica Ultrasil 7005 by Evonik. Ultrasil 7005 is widely used as reinforcing filler in the rubber industry. For that purpose, morphology, DBP absorption, aggregate size distribution, and dispersing ability were investigated. SEM images shown in Figure 8 indicate a very similar structure of the observed fillers at all three magnification levels.

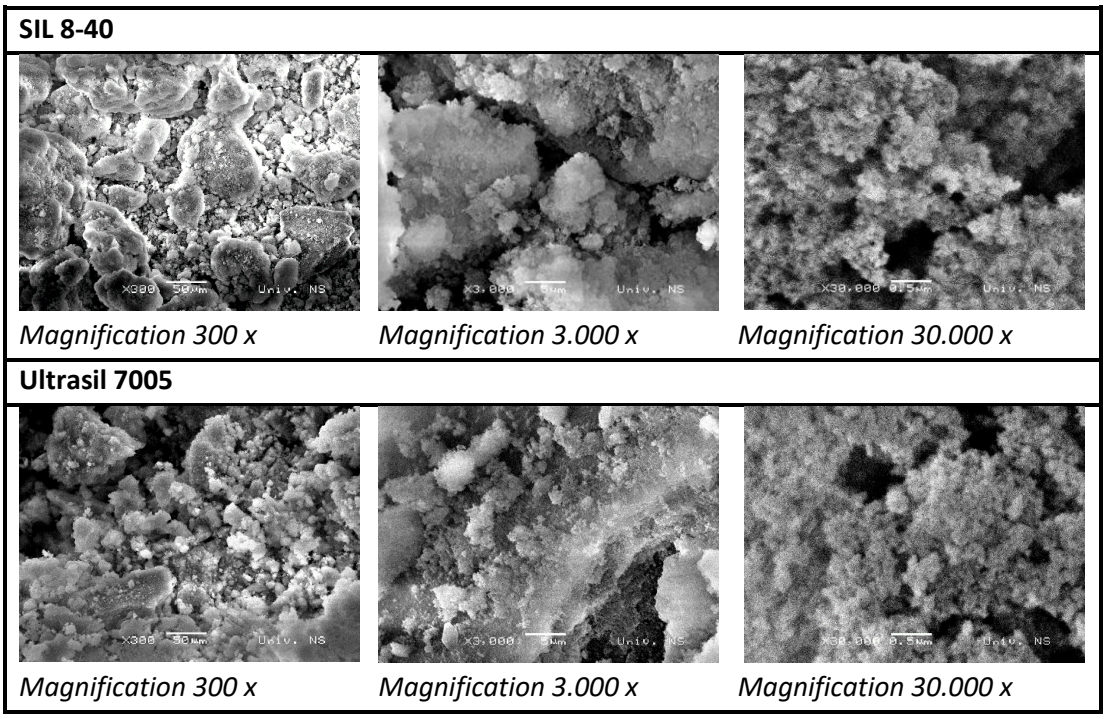

Figure 8. SEM images of SIL 8-40 and Ultrasil 7005

DBP absorption of two powders is listed in Table 3, while aggregate size distribution is shown in Figure 9. Figure 9 reveals that the two powders have similar median particle diameters. Ultrasil 7005 has narrower particle size distribution, while SIL 8-40 has a slightly greater content of finer particles. Obscuration dependence on sonication time of silica powders in aqueous suspension is shown in Figure 10 and it can be seen that SIL 8-40 shows a breakup trend similar to Ultrasil 7005.

Table 3. DBP absorption of silica fillers

Silica powder	SIL 8-40	Ultrasil 7005
DBP absorption (ml/g)	2,61	2,38

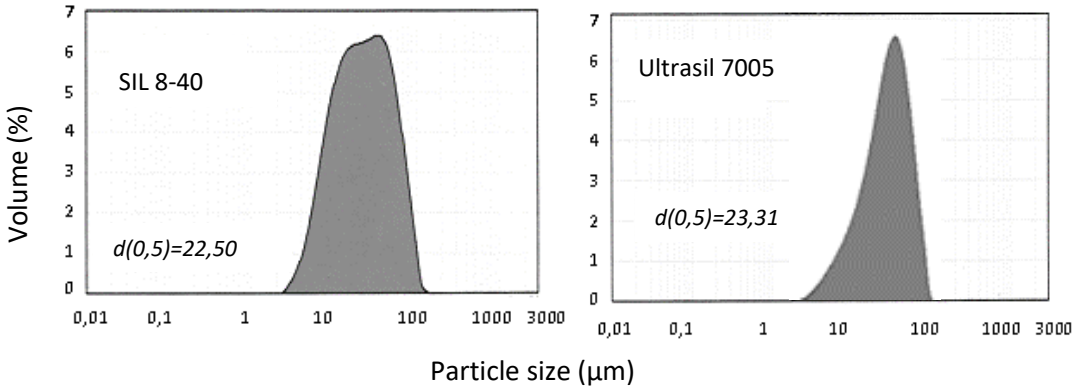

Figure 9. Aggregate size distributions of SIL 8-40 and Ultrasil 7005

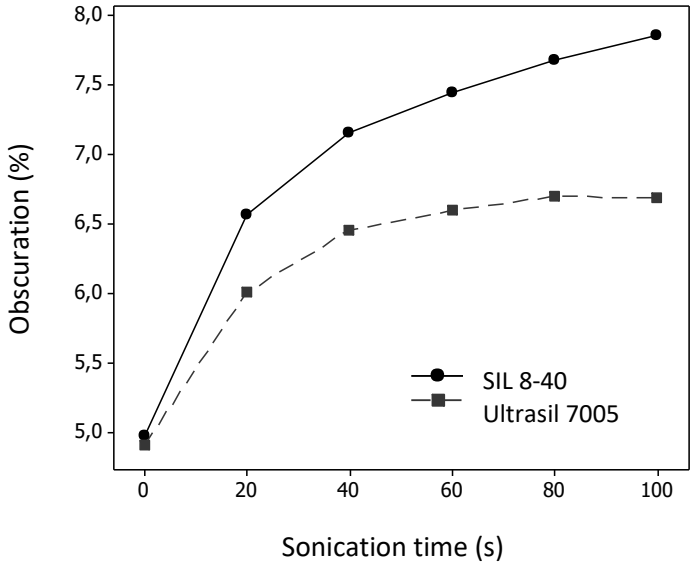

Figure 10. Effect of sonication time on Ultrasil 7005 and SIL 8-40

3.2. Properties of filled elastomers

3.2.1. The cure characteristics of filled elastomers

The vulcanization characteristics and important mechanical characteristics of rubber composites containing SIL 8-40 and Ultrasil 7005 were also investigated. The cure characteristic of natural rubber (NR) samples filled with Ultrasil 7005 and SIL 8-40 are shown in Table 4 and corresponding cure curves are shown in Figure11.

Table 4. Characteristic parameters of vulcanization

Composite	Torque momentum (dNm)			Vulcanization time (s)					Scorch time (s)		Cure rate index (s^{-1})
	M_L	M_H	M_H-M_L	t_{10}	t_{30}	t_{50}	t_{60}	t_{90}	t_{s1}	t_{s2}	CRI
NR/Ultrasil 7005	4,4	25,4	21,0	64	73	80	85	139	48	64	1,33
NR/SIL 8-40	5,0	24,6	19,6	70	80	90	107	166	51	70	1,04

The cure curves depicted in Figure 11 indicate that rubber samples filled with Ultrasil 7005 and SIL 8-40 have similar vulcanization characteristics. Rubber filled with SIL 8-40 has a slightly higher min. torque and lower max. torque, as well as shorter vulcanization time and longer scorch time.

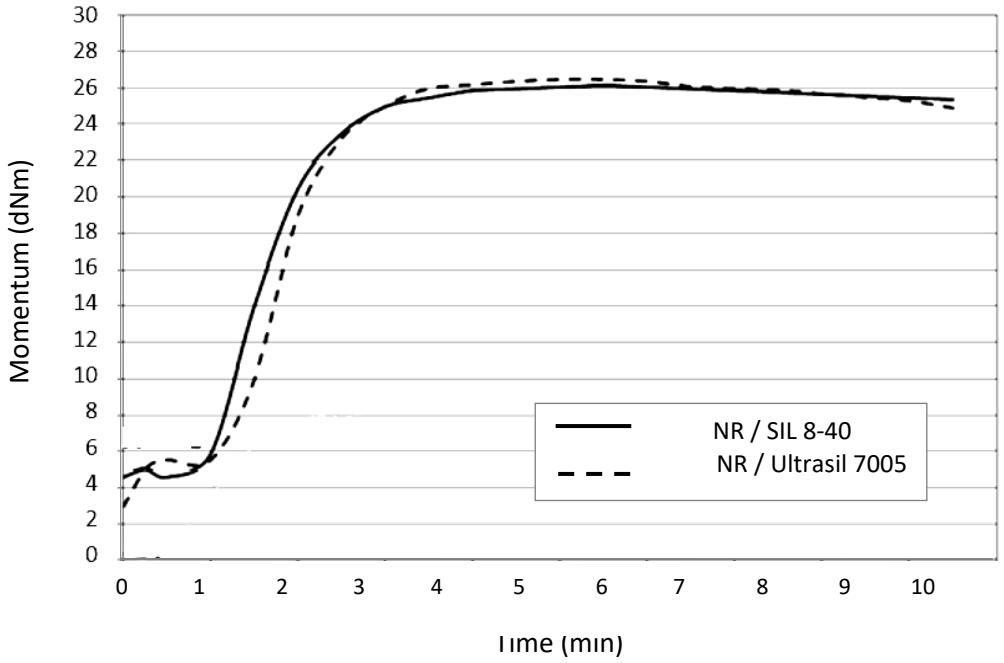

Figure 11. Rheographs of filled elastomers

3.2.2. Mechanical properties of filled elastomers

The mechanical properties of NR/Ultrasil 7005 and NR /SIL 8-40 composites were summarized in Table 5.

Table 5. Mechanical properties of filled elastomers

Composite	Tensile strength (MPa)	Elongation at break (%)	Modulus at 300% elongation (MPa)	Hardness (°ShA)	Abrasion resistance (mm^3)
NR/Ultrasil 7005	21	525	9,5	68,5	136
NR/SIL 8-40	19,5	505	10	68,5	128

The results show that the mechanical properties of NR/Sil 8-40 composites are close to that of NR/Ultrasil 7005 composites. NR/Ultrasil 7005 composite has slightly higher tensile strength, elongation at break, and abrasion resistance, while NR/Sil 8-40 composite has higher modulus. Two composites have identical shore hardness. Based on the presented comparative results, it was confirmed that highly effective rubber reinforcing filler can be produced by the proposed carbonation method.

4. Conclusion

In this work, the possibility of obtaining high-quality silica reinforcing filler by carbonation of sodium silicate solution was investigated. SEM analyses show that precipitated silica morphology largely depends on the reaction temperature and SiO_2 concentration in dilute sodium silicate solution. Silica precipitated at 40 °C from the solution containing 8 % of SiO_2 had the highest DBP absorption, as well as the best dispersion ability in an aqueous solution. Comparative tests of silica obtained at these conditions with commercial reinforcing filler Ultrasil 7005 (Evonik) shown that two fillers have similar properties. Also, results of tests conducted on

rubber compounds filled with two fillers indicate similar cure characteristics and mechanical properties. These results show that silica precipitated by the proposed method has great potential to be used as reinforcing filler for rubber.

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