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Novel precipitated silicas: an active filler of synthetic rubber

**Teofil Jesionowski · Andrzej Krysztafkiewicz ·
Jolanta Żurawska · Karol Bula**

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Abstract Highly dispersed silicas have been obtained at a semi-technical scale by precipitation from sodium metasilicate solutions using appropriately diluted solutions of ammonium hydrogencarbonate or ammonium chloride. The difference, as compared to the generally applied technology of silica precipitation using acids or their anhydrides, has been the involvement of the precipitation reaction in alkaline media. Attempts have been made at changing the silica surface character from hydrophilic to more hydrophobic, using a modifier from the group of silane coupling agents. The alkoxysilanes modifiers contained groups with chemical affinity towards functional groups of butadiene–styrene rubber. Modification of silica surface using silane coupling agents has been found to improve the reinforcement of vulcanizates, by increasing the tensile and tear strength in particular.

Introduction

Development of several branches of modern industry requires application of highly dispersed silicas, including applications in food industry, pharmaceutical and cosmetic products, in which they serve as densifying agents and, in toothpastes as abrasiveness improving agents [1, 2]. Moreover, highly dispersed silicas used as fillers of rubber vulcanizates improve their resistance to chemicals and their mechanical strength. The reinforcing effect of fillers includes the increase in tensile strength, abrasion resistance and tear strength of elastomers [3–6].

The factors which significantly affect mechanical properties of vulcanizates include crosslinking density, type of network knots, the hydrodynamic effect, filler–polymer interactions and the related extent of dispersion of the mixture components [3, 7–17]. The amount of bound rubber used as a measure of the filler/polymer interactions [18]. The extent of filler/filler interactions can be determined by, e.g. measurements of the dynamic modulus of the rubber samples [4, 5, 19]. When applying this method, the elastic component is determined for a small deformation since increase in sample deformation is accompanied by destruction of spatial network of the filler in the rubber.

The fillers applied in polymer processing should be fully chemically neutral to the polymer and to the accessory agents applied, should be thermostable, capable of rapid and easy dispergation in the polymer matrix, should adsorb insignificant amounts of softeners, should not deteriorate the mechanical properties of the material and should be white in colour, possibly uniform and relatively inexpensive.

Silica fillers exhibit hydrophilic surface while most of polymers have hydrophobic properties [20]. The differences in the chemical and physicochemical character between the organic binder and inorganic mineral or synthetic filler imply that adhesion forces play insignificant role in the integration of these components. Appropriate modification of the filler/polymer interface can result in enhancement of the forces of their interaction and, in consequence, in improvement of the properties of the polymer [21–24]. In production of the filled polymer composites, their reciprocal interaction requires that the

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T. Jesionowski (✉) · A. Krysztafkiewicz · J. Żurawska
Institute of Chemical Technology and Engineering, Poznan
University of Technology, M. Sklodowskiej-Curie 2 sq.,
60-965 Poznan, Poland
e-mail: teofil.jesionowski@put.poznan.pl

K. Bula
Institute of Materials Technology, Poznan University
of Technology, Piotrowo 3 St., 60-965 Poznan, Poland

filler should be wetted by the polymer, which would permit adsorption of the polymer on filler particles and their mutual interaction [25–28]. The improvement is a measure of the strengthening effect obtained as a result of the use of active fillers. The achievement of the desired effects depends on the dispersion, structure, specific surface area, the interface phenomena reflecting the character of the surface, extent of filler dispersion in the rubber, physical and chemical character of the surface.

Apart from dispersion, the granulometric composition is also of importance and it should be possibly uniform. The presence of even a low number of large particles (e.g. secondary agglomerates) has an evident unfavourable effect on physicochemical properties of vulcanizates. Larger size particles certainly disturb the equilibrium of vulcanizate structure, deteriorate to a variable extent their physicomechanical indices, and moreover, such particles may not be adhesive to the rubber.

The modified and unmodified silicas were used as fillers of the butadiene–styrene rubber, of the trade name KER 1500. The principal property of the rubber involves its high elasticity. The optimum use of this property had been impossible before development of the rubber stabilization method by sulphur vulcanization, involving crosslinking of rubber polymer chains, e.g. by disulphide bridges.

Experimental

Preparation of hydrated silicas

Highly dispersed silicas were obtained by precipitation from aqueous solutions of sodium metasilicate, $Na_2O \cdot mSiO_2 \cdot nH_2O$ made by VITROSILICON S.A. (modulus 3.3 and density of 1.39 g cm^{-3}), using a 5 wt% NH_4HCO_3 or NH_4Cl solution (v/v ratio of the solutions—1:2) both produced by POCh S.A. The difference between the reaction proposed and the classical techniques of silica precipitation, using acids or acid anhydrides, was that the precipitation reaction was always performed in an alkaline medium. The reaction of silica formation in the presence of ammonium salts followed the general equation of

$$\begin{aligned}&Na_2O \cdot mSiO_2 + 2NH_4^+ + nH_2O\\&\quad\rightarrow mSiO_2 \cdot (n+1)H_2O + 2Na^+ + 2NH_3\end{aligned}$$

The reactor of 50 dm^3 in capacity, equipped with a propeller top stirrer, was loaded with a 5 wt% water solution of the precipitating agent, NH_4HCO_3 or NH_4Cl, and a hydrophobicity-inducing agent, Rokafenol N9—$C_9H_{19}PhO(CH_2CH_2O)_nH$, where mean $n \cong 9$ (PCC ROKITA S.A.), in the amount of 1 weight part/100 weight parts of silica. Using a thermostat, a constant temperature of 85 °C was maintained when ammonium chloride or of 25 °C when ammonium hydrogencarbonate was used as the precipitating agent.

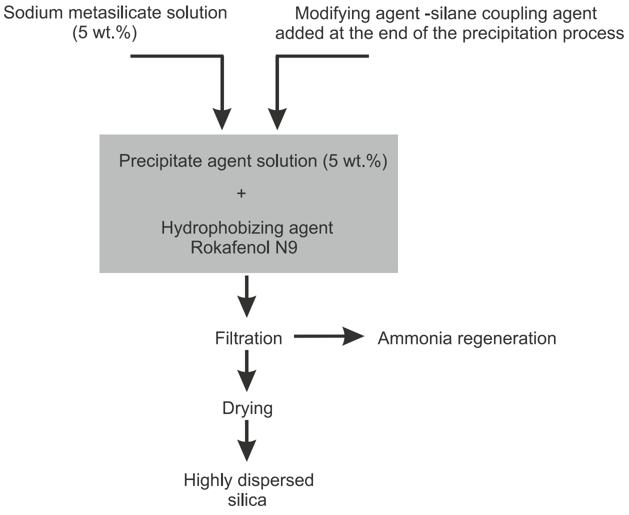


Fig. 1 Scheme illustrating the process of obtaining modified highly dispersed silicas

To the so-prepared precipitation system, a 5% solution of sodium metasilicate was dosed. The rate of dosing the sodium metasilicate solution was set at 1 dm^3 h^{-1}. The system was intensely stirred. The pH of 8–9 was established as optimum at which the silica precipitation process was stopped. The average duration of silica precipitation was 5 h.

Moreover, modification of the hydrated silica surface was performed during the process of its precipitation, using the wetting technique in the course of 30 min. The experiments were based on our earlier established optimum parameters for silica precipitation [29]. Three types of silane coupling agents were used in the amount of 3 weight parts/100 weight parts of silica: 3-mercaptopropyltrimethoxysilane (A-189) from Sigma-Aldrich, 3-methacryloxypropyltrimethoxysilane (U-511) and *N*-2-(aminoethyl)-3-aminopropyltrimethoxysilane (U-15) both made by UniSil.

The scheme of highly dispersed silica precipitation with the use of the modifying agents is presented in Fig. 1.

Physicochemical properties of the silicas obtained

Following the precipitation, the silicas were subjected to physicochemical tests, in which their bulk densities as well as water, dibutyl phthalate and paraffin oil absorbing capacities were estimated. The bulk densities were determined using a WE-5 electromagnetic volumeter.

Morphology and microstructure of the silicas were analysed to characterize the dispersion, particle shape and morphology of the particles, and the agglomerates structure silica aggregation and agglomeration type as a result of precipitation. The studies were performed using scanning electron microscopy (SEM). The observations were made using a Phillips SEM 515 microscope. Size distribution of silica particle agglomerates and aggregates were also estimated using a ZetaPlus instrument (Brookhaven Instruments Inc.) by the dynamic light scattering (DLS) method. The specific surface areas as well as isotherms of nitrogen adsorption/desorption on silica surface were established using an ASAP 2010 apparatus (Micromeritics Instruments Co). Elemental analyses of the modified silica samples were performed using a Vario EL III apparatus (Elementar). The results obtained permitted calculation of the surface coverage extent using the equation of Berendsen and de Golan [30]. Spectroscopic tests were conducted by FT-IR technique using an EQUINOX 55 apparatus (Brucker). The unmodified and modified silicas were used as fillers of rubber blends. The blends were composed of butadiene–styrene rubber, KER 1500—100 weight parts, stearic acid—3 weight parts, silica—50 weight parts, ZnO—5 weight parts, DM accelerator (dibenzothiazole disulphide)—0.8 weight part, D accelerator (*N′N*-diphenylguanidine)—1.8 weight parts, sulphur—2.5 weight parts. The reference sample was Ultrasil VN3 silica made by Evonik.

The vulcanization was performed in 20 min, at a temperature of 145 °C. Moreover, mechanical properties of the vulcanizates obtained were estimated, including tensile strength, tear strength, elasticity and hardness. In addition, increase in temperature and endurance upon compression repeated at the frequency of 30 Hz was also measured.

Results and discussion

The studies aimed at obtaining silicas manifesting low bulk density, high capacity to absorb paraffin oil and the presence of highly dispersed particles of a possibly uniform character.

Principal physicochemical parameters of the unmodified silicas, precipitated using NH_4HCO_3 or NH_4Cl solution on a semi-technical scale, and those of the silicas modified using three types of silane coupling agents are presented in Table 1.

Silicas precipitated using pure ammonium salts (and the silica precipitated using ammonium chloride solution in particular) manifested relatively low activity, which is reflected by the data of Table 1: the relatively low capacity to absorb paraffin oil and high bulk density. Application of non-ionic surfactant in the course of silica precipitation by ammonium salts evidently improved the physicochemical properties of the silicas. Independent of the type of ammonium salt employed, the capacity to absorb paraffin oil and specific surface areas clearly increased, while their bulk density diminished. Isotherms of nitrogen adsorption/desorption of the silicas examined precipitated using ammonium chloride solution are compared in Fig. 2a. The isotherm corresponding to the silica precipitated with pure NH_4Cl solution, with no supplements, had an almost flat shape, and the increase in partial pressure was not accompanied by evidently enlarged amounts of nitrogen adsorbed on silica surface. Such a course of the isotherm

Table 1 Principal physicochemical properties of the unmodified silicas precipitated using 5% solutions of NH_4Cl or NH_4HCO_3 and of the silicas modified using silane coupling agents at a semi-technical scale

Filler type	Capacity to absorb water (cm^3 100 g^{-1})	Capacity to absorb dibutyl phthalate (cm^3 100 g^{-1})	Capacity to absorb paraffin oil (cm^3 100 g^{-1})	Bulk density (g dm^3)	Specific surface area (m^2 g^{-1})
NH_4Cl					
–	350	500	650	110	65
1 wt/wt of Rokefenol N9	500	950	1,300	45	230
1 wt/wt of Rokefenol N9 + 3 wt/wt of A-189	300	700	1,000	90	225
1 wt/wt of Rokefenol N9 + 3 wt/wt of U-511	250	800	1,150	60	220
1 wt/wt of Rokefenol N9 + 3 wt/wt of U-15	400	750	1,060	55	210
NH_4HCO_3					
–	350	750	1,000	80	140
1 wt/wt of Rokefenol N9	700	850	1,200	50	250
1 wt/wt of Rokefenol N9 + 3 wt/wt of A-189	600	750	1,150	65	230
1 wt/wt of Rokefenol N9 + 3 wt/wt of U-511	650	850	1,500	60	220
1 wt/wt of Rokefenol N9 + 3 wt/wt of U-15	750	800	1,450	70	220

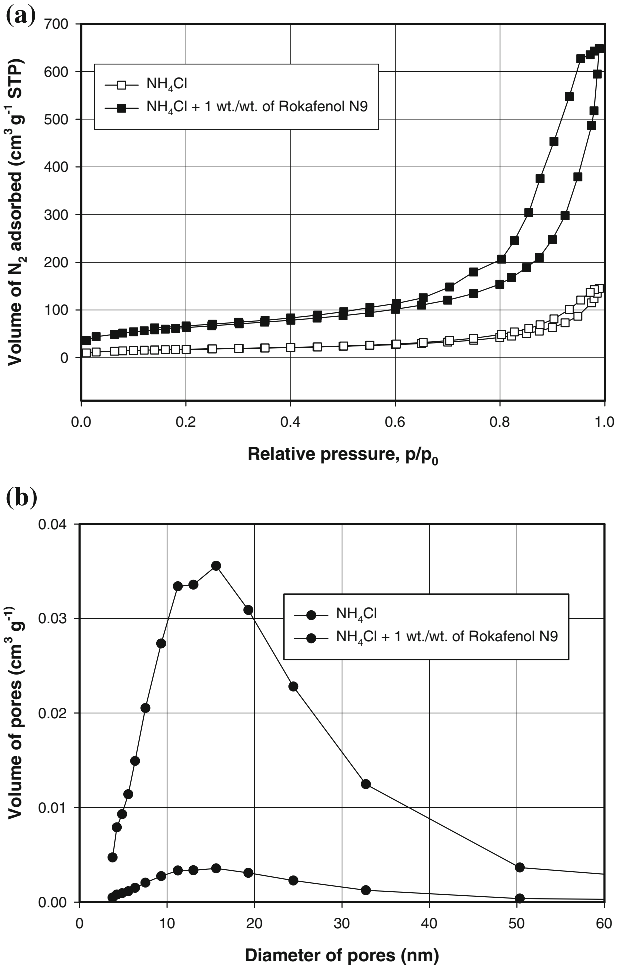


Fig. 2 N_2 adsorption/desorption isotherms (**a**) and pore size distribution (**b**) of silicas precipitated with NH_4Cl solution

pointed to very low activity of the silica: the amount of adsorbed nitrogen did not exceed 150 $cm^3\ g^{-1}$ at the maximum relative pressure of 1.0. On the other hand, in the case of silica precipitated in the presence of 1 wt/wt of Rokafenol N9, the isotherm clearly increased within the range of relative pressures of 0.7–1.0. The amount of nitrogen adsorbed at $p/p_0 = 1$ did not exceed 650 $cm^3\ g^{-1}$; the effect obtained provided a significant evidence for a marked increase in activity of silica precipitated in the presence of non-ionic surfactant. The courses of the two isotherms indicated that the silicas belonged to mesoporous substances (the volume of nitrogen adsorbed did not increase until high values of relative pressure were reached, exceeding the value of 0.7).

The data on changes in the morphological structure of silicas could also be obtained from analysis of pore size distribution by BJH technique, presented in Fig. 2b.

Isotherms of nitrogen adsorption/desorption of silicas precipitated using ammonium hydrogencarbonate are compared in Fig. 3. Upon adsorption of N_2 on the surface of the silica precipitated using a pure NH_4HCO_3 solution and on the surface of the silica precipitated in the presence of 1 wt/wt of Rokafenol N9, using propeller top stirrer, a clearly observed increase in the amount of the nitrogen adsorbed was noted accompanied by rising relative pressure in the relative pressure range of 0.7–1.0. At $p/p_0 = 1.0$, the amount of nitrogen adsorbed reached 500–600 $cm^3\ g^{-1}$, which evidenced high activity of the silicas precipitated using an NH_4HCO_3 solution. The obtained data show that higher activity of silicas was obtained using an NH_4HCO_3 solution to initiate precipitation.

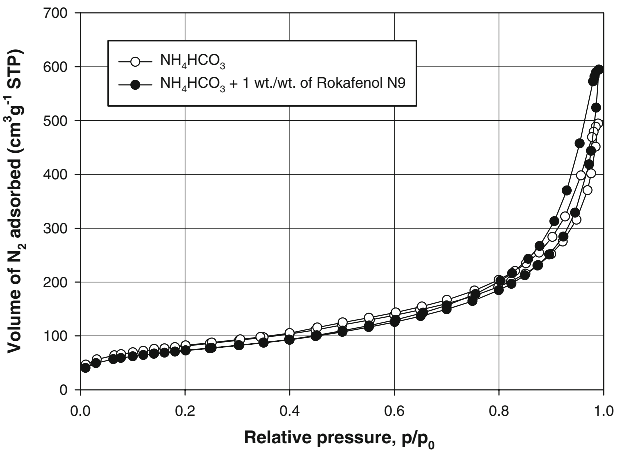
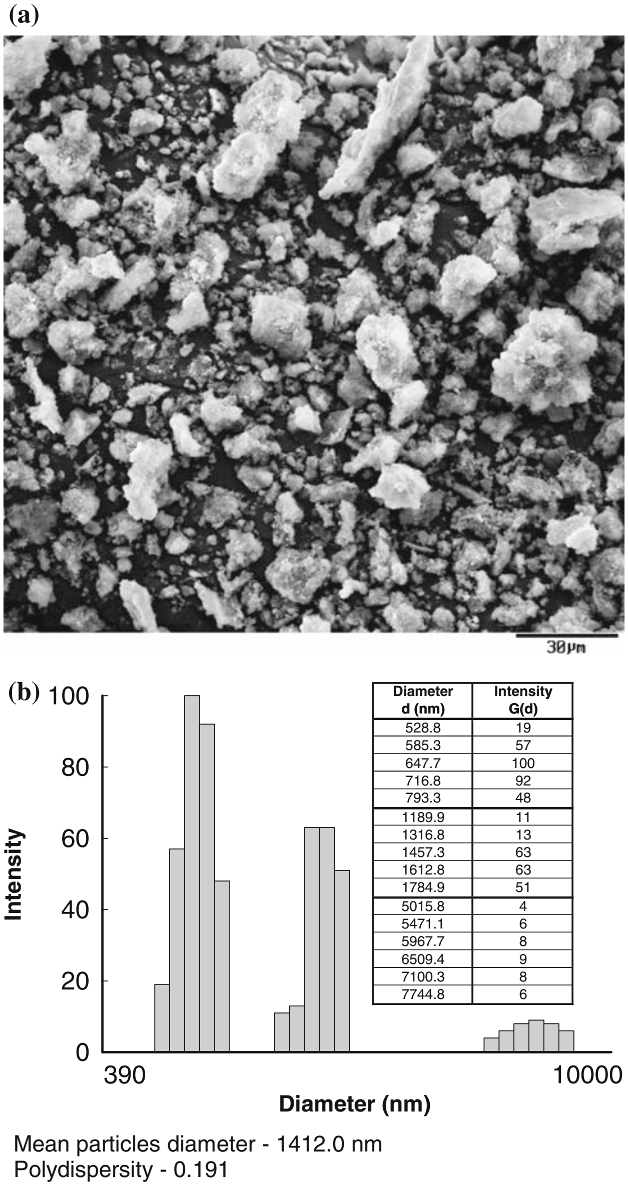


Fig. 3 N_2 adsorption/desorption isotherms of silicas obtained with NH_4HCO_3 solution

The silica precipitated using a pure NH_4Cl solution manifested the presence of relatively large particles with a clear tendency to form agglomerates. In the particle size distribution (Fig. 4b), an intense band was present, linked to primary agglomerates in the range of 529–793 nm (maximum intensity of 100 corresponded to the primary agglomerates of 647.7 nm in diameter), and two bands of lower intensity in the ranges 1,190–1,785 nm (maximum intensity of 63 corresponded to the agglomerates of 1,457.3 nm in diameter) and 5,016–7,745 nm (maximum intensity of 9 corresponded to the agglomerates of 6,509.4 nm in diameter), representing secondary agglomerates.

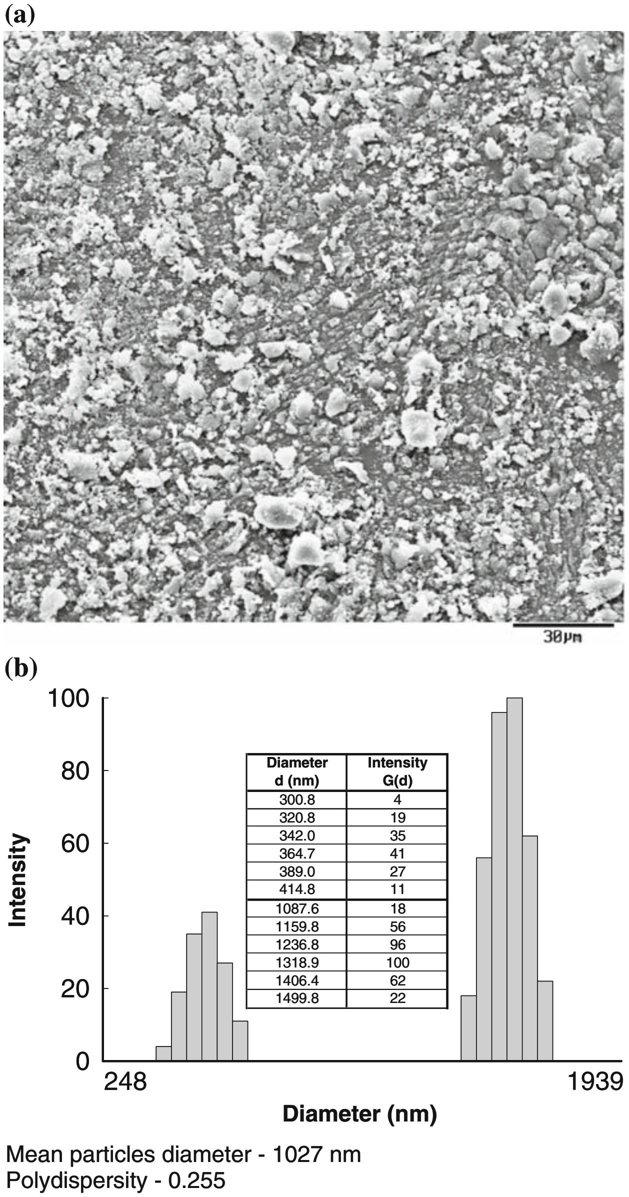
The silica precipitated at room temperature using NH_4HCO_3 exhibited a tendency to form agglomerates, which is evident from Fig. 5a (SEM microphotograph) showing particle agglomerates and individual fine aggregates. The particle size distribution (Fig. 5b) manifested an evident broad band in the range of 1,088–1,500 nm (maximum intensity of 100 corresponded to the agglomerates diameter of 1,318.9 nm). The band was typical of secondary agglomerates in the precipitated silicas. The particle size distribution showed a less intense band



Diameter d (nm)	Intensity G(d)
528.8	19
585.3	57
647.7	100
716.8	92
793.3	48
1189.9	11
1316.8	13
1457.3	63
1612.8	63
1784.9	51
5015.8	4
5471.1	6
5967.7	8
6509.4	9
7100.3	8
7744.8	6

Mean particles diameter - 1412.0 nm
Polydispersity - 0.191

Fig. 4 SEM photo (**a**) and particle size distribution (**b**) of silica precipitated with NH_4Cl solution



Diameter d (nm)	Intensity G(d)
300.8	4
320.8	19
342.0	35
364.7	41
389.0	27
414.8	11
1087.6	18
1159.8	56
1236.8	96
1318.9	100
1406.4	62
1499.8	22

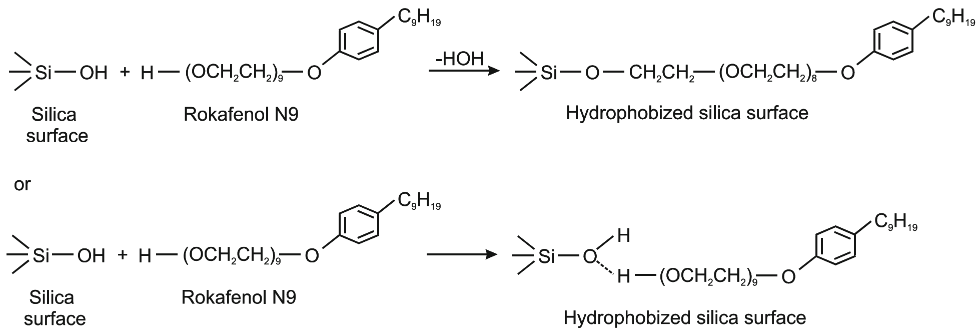
Mean particles diameter - 1027 nm
Polydispersity - 0.255

Fig. 5 SEM image (**a**) and particle size distribution (**b**) of silica precipitated with NH_4HCO_3 solution

assigned to primary agglomerates of 301–415 nm in diameter (maximum intensity of 41 corresponded to aggregates of 364.7 nm in diameter).

The hydrophobicity-inducing agent has been found to exert a significant effect on the quality of final products. Definitely, the most effective proved to be the addition of Rokafenol N9. The improvement in the physicochemical properties of silicas as a result of addition of a hydrophobicity-inducing agent may follow from the blocking of centres (silanol groups) on the surface of developing silica particles. When silica precipitates in the absence of hydrophobicity-inducing agents, water molecules become adsorbed on the surface of silica. The presence of the attached molecules of hydrophobicity-inducing agent means that the neighbouring silanol groups on silica surface are unable to bind water molecules on the surface. Hence, the process of agglomerate formation is considerably blocked (a decreased tendency to agglomerate formation is observed) as compared to the system obtained in the absence of the hydrophobicity-inducing agent. Moreover, addition of the hydrophobicity-inducing agent in the course of silica precipitation causes loosening of the silica structure, disturbs the process of mass transfer to the surface of silica particles, which results in inhibition of growth in size of silica particles, and in effect, the silica is precipitated in the form of very fine particles. Silica particles depart from each other as a result of adsorption of hydrophobicity-inducing agent, distances between the particles increase, and thus, hydrogen bonds between individual silanol groups are weakened. In effect, this promotes an increase in the specific surface area of silica and, first of all, an increase in the volume of nitrogen adsorbed on the surface. Therefore, decomposition of aggregates and agglomerates takes place, and silica particles become more uniform which is important for their application as fillers of plastomers and elastomers.

The mechanism of surfactants activity may involve a chemical reaction of a silica surface silanol group with the hydroxyl group of Rokafenol N9 or hydrogen bond formation between the hydroxyl groups on the silica surface and those of the hydrophobicity-inducing agent. The reactions proposed are as follows:



The direct proof of the reaction course might be the observed absence of secondary agglomerates in the case of silica precipitated with ammonium chloride in the presence of 1 wt/wt of Rokafenol N9. The particle size distribution (Fig. 6b) indicated exclusively the presence of primary agglomerates with a noted tendency towards decreasing diameter, reaching 824.6 nm. Moreover, the only band present in the distribution covered a wide range of agglomerate diameters of 422–1,334 nm (maximum intensity of 100 corresponded to primary agglomerates of 749.9 nm in diameter).

Changes in the particle size and morphology of silica precipitated using NH_4HCO_3 solution in the presence of the 1 wt/wt of Rokafenol N9 are illustrated in Fig. 7. The almost ideally uniform structure of the precipitated silica could fully correlated with its desirable physicochemical parameters is noted. Silicas precipitated in such conditions manifested highly uniform character, which was confirmed by a respective SEM microphotograph (Fig. 7a). The particle size distribution (Fig. 7b) shows a single band of high intensity covering a narrow range of low diameters of primary agglomerates, 1,123–1,148 nm (maximum intensity of 100 corresponded to the primary agglomerates of 1,143.2 nm in diameter). As compared to the silica precipitated in the absence of hydrophobicity-inducing agents (Fig. 5), the silica precipitated in the presence of 1 wt/wt of Rokafenol N9 manifested a slightly higher mean diameter of particle agglomerates, of 1,140 nm. However, the intense band was shifted towards lower particle diameters and the obtained product manifested a perfectly uniform character, as expressed by the polydispersity index of 0.005.

Modification of silica surface with silane coupling agents insignificantly affected the morphology of the fillers; usually, it enhanced uniformity of the silicas and caused a decrease in the mean particle diameter. The particle size distribution of silica modified with 3 wt/wt of mercaptosilane A-189 presented an intense band, representing primary agglomerates, in the range of 862–879 nm (maximum intensity of 100 corresponded to the agglomerates of 874.7 nm in diameter; Fig. 8b). In the so-precipitated silica, the mean diameter of particle agglomerates was relatively low and amounted to 873.2 nm. The SEM photo (Fig. 8a) illustrated broken secondary agglomerates and primary particles.

The silica surface modification using silane coupling agents was evaluated on the basis of the elemental analysis determining the contents of carbon, nitrogen, hydrogen and sulphur, introduced to the silica surface and the silica surface coverage.

The silica surface coverage was calculated using the relationship proposed by Berendsen and de Golan [30]. Examples of percent contents of C, N, H and S and the coverage of the surface for modified silicas precipitated using NH_4HCO_3 solution in the presence of 1 wt/wt of Rokafenol N9 are presented in Table 2.

Exemplary FT-IR spectra (in the range of 2,500–4,000 cm^{-1}) of the silica precipitated using an NH_4Cl solution in the presence of Rokafenol N9 and the silica modified with 3 wt/wt of mercaptosilane A-189 are given in Fig. 9. Figure 9a presents the broadened band at 3,200–3,750 cm^{-1}, corresponding to the silica surface silanol groups and water adsorbed on the silica surface. Since the silica samples tested were dried only at 105 °C, the band at

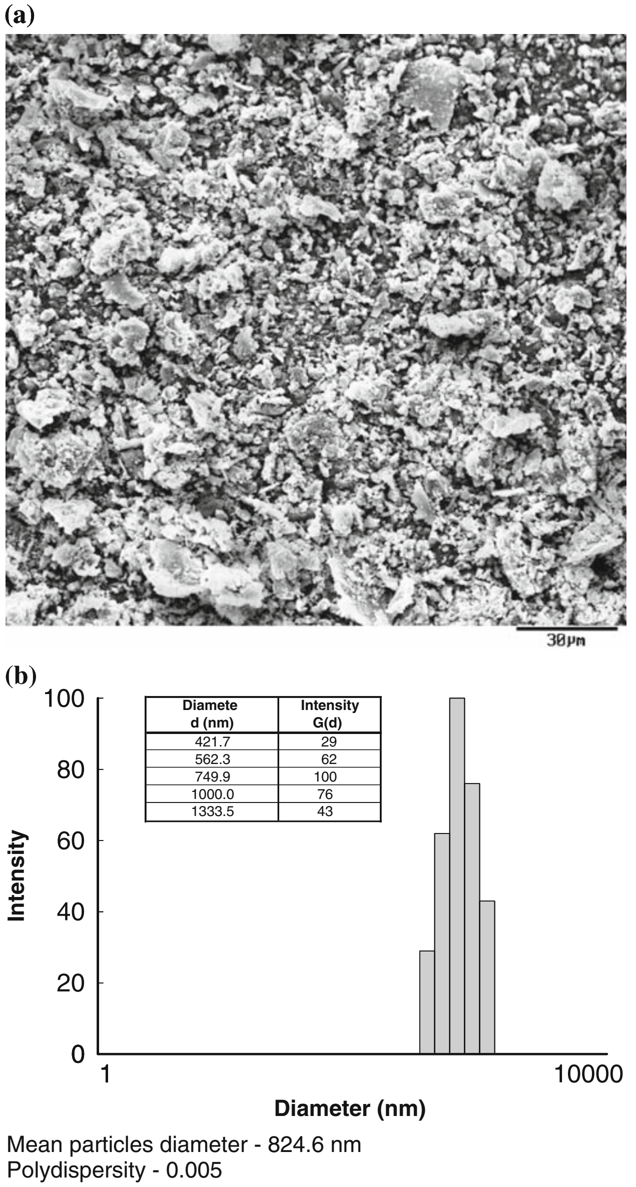


Fig. 6 SEM photo (**a**) and particle size distribution (**b**) of silica precipitated with NH_4Cl solution in the presence of 1 wt/wt of Rokafenol N9

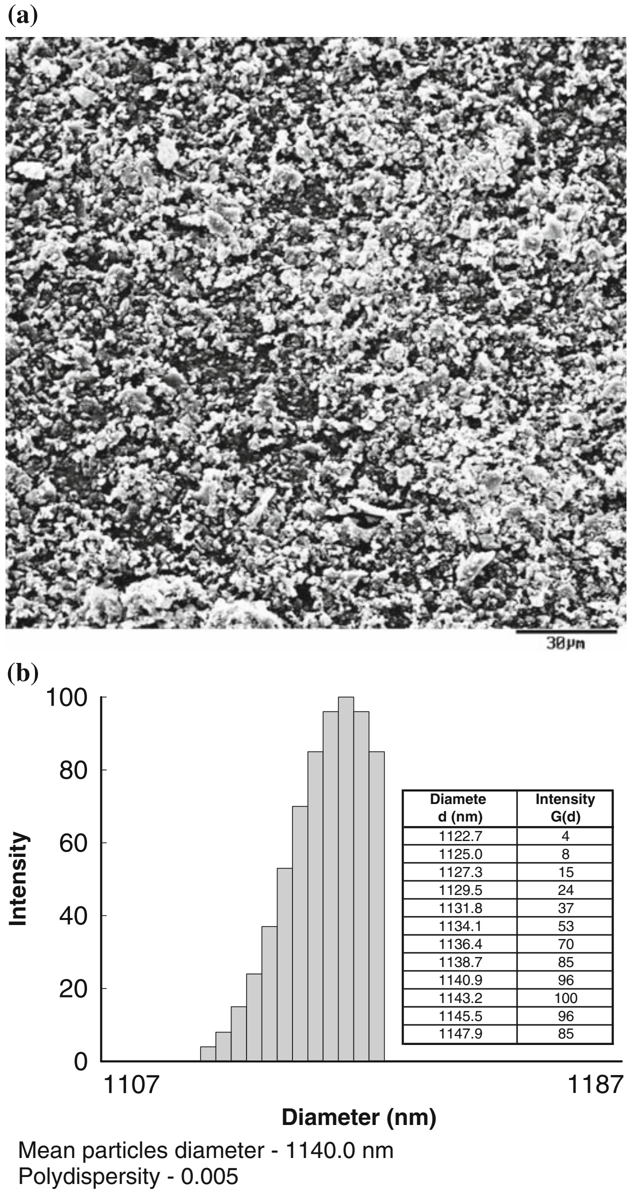
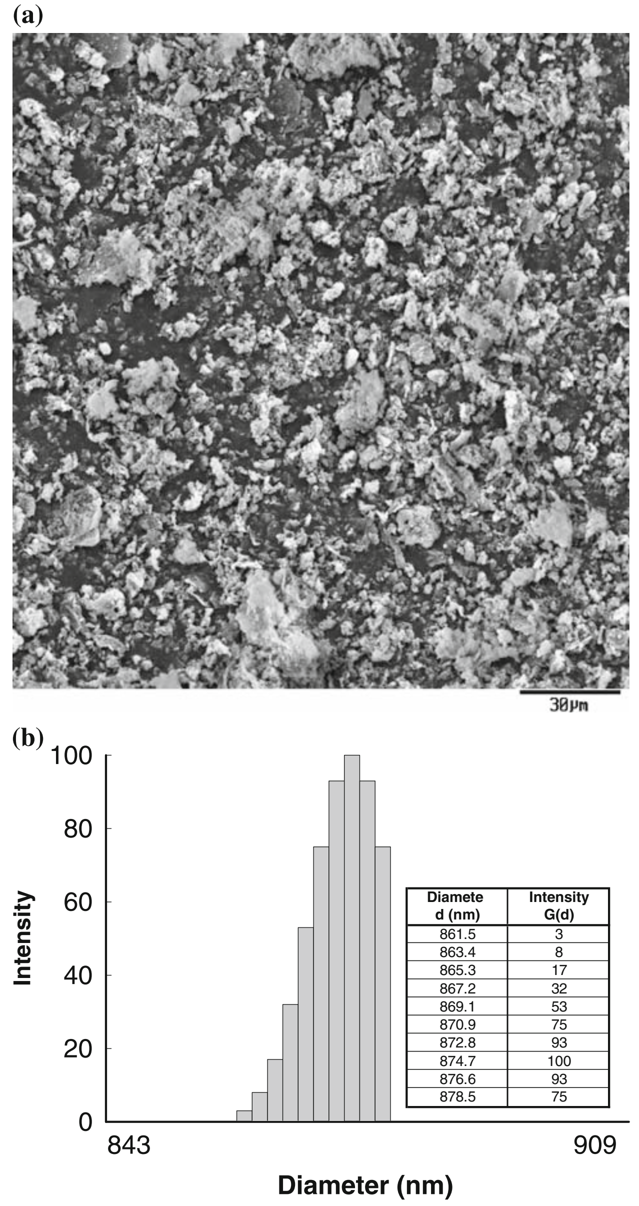


Fig. 7 SEM image (**a**) and particle size distribution (**b**) of silica precipitated with NH_4HCO_3 solution in the presence of 1 wt/wt of Rokafenol N9

3,660 cm^{-1} typical of vicinal silanol groups was disturbed by the band assigned to the physically bound water at around 3,440 cm^{-1}. The spectra presented reveal a minimum effect of the loss of silanol groups and water adsorbed (i.e. decreased intensity of these bands) for mercaptosilane-modified silicas. As indicated by the data of Fig. 9a, it was very difficult to appraise the loss of the silanol groups (at 3,660 cm^{-1}) on the mercaptosilane-modified surface. The silicas dried at 105 °C still continued on their surface-significant amounts of physically adsorbed water. For this reason, determination of silanol group concentration on silica surface was performed for the samples calcined at 650 °C for 2 h.

Figure 9b shows a very sharp band corresponding to the silanol groups on the silica surface (at 3,660 cm^{-1}). The intensity of this band was evidently lower for the silica modified with 3 wt/wt of mercaptosilane, as compared to that of the same band obtained for the unmodified silica. This demonstrated that the modification resulted in a decreased amount of silica surface silanol groups. The decrease in silanol groups following the modification with mercaptosilane was very significant and pointed to the

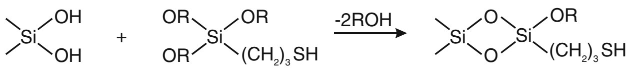


Diamete d (nm)	Intensity G(d)
861.5	3
863.4	8
865.3	17
867.2	32
869.1	53
870.9	75
872.8	93
874.7	100
876.6	93
878.5	75

Mean particles diameter - 873.2 nm
Polydispersity - 0.005

Fig. 8 SEM photo (**a**) and particle size distribution (**b**) of silica precipitated with NH_4HCO_3 solution in the presence of 1 wt/wt of Rokafenol N9 and modified with 3 wt/wt of A-189 silane

reaction of condensation between the groups on silica surface and alkoxy groups of the modifier:



In the reaction of condensation with mercaptosilane, only a fraction of surface silanol groups participated. Nevertheless, calculation of the extent of the reaction between the silica surface silanol groups and silane alkoxy groups on the grounds of the IR spectra obtained was very difficult and the results were inaccurate. However, the decreased intensity of the 3,660 cm^{-1} band might indicate the occurrence of a chemical reaction of modification on the silica surface.

Thus, the surface modification of silica using silanes (containing various functional groups) reduced markedly the density of OH groups on the silica surface. This resulted in a more pronounced hydrophobicity of the silica and permitted a reaction between the filler and the polymer thanks to the appearance on the surface of novel organic functional groups, e.g. mercaptane group, vinyl group, methacryl group.

The modulus of the vulcanizates obtained related to the extent of deformation is shown in Table 3. Tables 3 and 4 present also the data characterizing the mechanical strength of the vulcanizates filled with the unmodified standard silica Ultrasil VN3.

As indicated by data of Table 3, the highest modulus characterizes the vulcanizate samples filled with the silica modified with 3 wt/wt of mercaptosilane. The unfilled vulcanizate manifested a very low 300% modulus—1.4 MPa. The vulcanizate filled with unmodified silica disrupted at the elongation at break of 500% and its modulus reached a very high value of 6.3 MPa. Similar values of modulus were obtained for the vulcanizates filled with the unmodified standard silica Ultrasil VN3.

The tests proved that the modification of silica surface with mercaptosilane has clearly improved the modulus of the vulcanizate. The vulcanizate did not disrupt until elongation at break of 600% was reached and the modulus reached a value of over 9 MPa.

Table 2 Elemental contents of N, C, H and S in the unmodified silicas and in the silicas modified using silane coupling agents, precipitated using NH_4HCO_3 solution in the presence of 1 wt/wt of Rokafenol N9 (at room temperature) and the extent of surface coverage

Modifier	Elemental content (%)				Extent of surface coverage (μmol m^{-2})
	N	C	H	S	
–	–	0.332	1.119	–	–
1 wt/wt of Rokefenol N9 + 3 wt/wt of A-189	–	0.708	1.332	0.142	0.180
1 wt/wt of Rokefenol N9 + 3 wt/wt of U-511	–	0.782	1.289	–	0.129

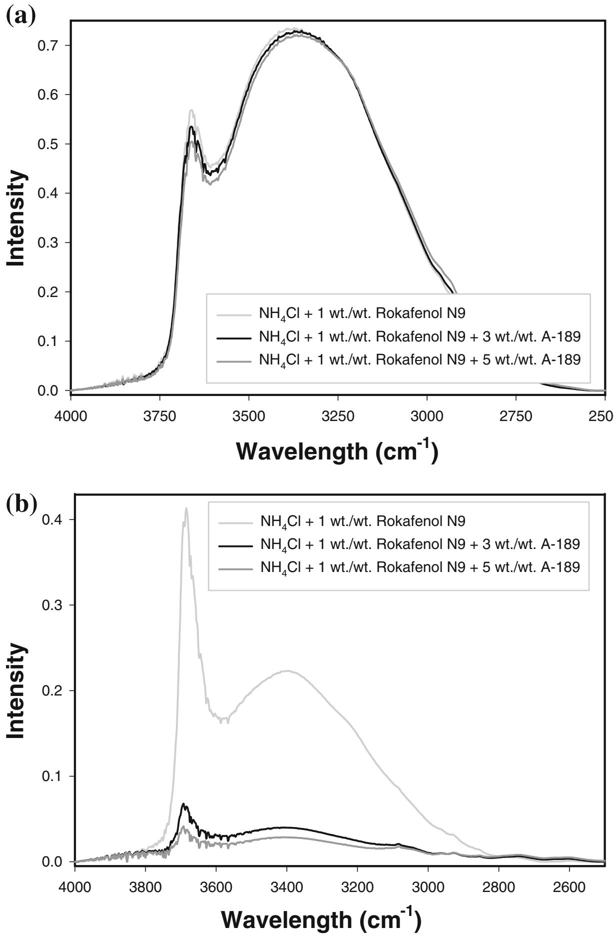


Fig. 9 FT-IR spectra of silicas unmodified and modified with A-189 silane, **a** after drying at 105 °C and **b** after heating at 600 °C

The remaining strength parameters of the vulcanizates studied are listed in Table 4, including tensile strength, tear strength, elasticity and Shore A hardness.

Tensile strength is a significant index of the reinforcing effect, dependent primarily on the extent of the filler dispersion in the mixture and on the chemical affinity of the filler to the polymer. It was also related to the value of the surface tension at the filler/polymer interface. Reduction of the tension by hydrophobic transformation and surface modification facilitates the solvation of its particles by the polymer and achievement of a desired homogenous character of the mixture.

Silica surface modification also exerted a significant effect on tensile strength, the principal index characterizing mechanical strength of a rubber. The unfilled vulcanizate manifested a very low tensile strength, equal to 1.55 MPa. Introduction of the unmodified filler to the rubber mixture increased its tensile strength to 7.62 MPa, and introduction to the mixture of aminosilane-modified silica resulted in the tensile strength of 10.32 MPa (Table 4). Modification of the silica surface using mercaptosilane also improved the tear strength, hardness according to Shore A and impact resilience of the product.

The tensile strength and tear strength of the vulcanizates filled with the standard silica Ultrasil VN3 are only slightly higher than the values obtained for the vulcanizates filled with the unmodified silica precipitated with ammonium hydrogencarbonate.

On the other hand, the elasticity of the filled vulcanizates decreased from the values of 52.3 to 46.9 in the case of vulcanizates filled with unmodified silica and to the value of around 51 for vulcanizates filled with silicas modified with aminosilane or methacryloxysilane. The vulcanizate filled with the unmodified silica precipitated using NH_4Cl manifested the elasticity of 48.1. The decrease in the elasticity following the filling of vulcanizates with the unmodified or silane coupling agent-modified silicas reflected the restricted freedom of movement of rubber

Table 3 Modulus of vulcanizates filled with precipitated unmodified or modified silicas (mean values of five measurements)

Vulcanizate containing unmodified or modified filler	Modulus (MPa)						
	Elongation at break (%)						
	50	100	200	300	400	500	600
NH_4HCO_3							
KER 1500 unfilled	0.488	0.755	1.061	1.366	–	–	–
KER 1500/50 phr SiO_2	1.198	1.924	3.314	4.570	5.532	6.334	–
KER 1500/50 phr SiO_2 modified with A-189	1.320	2.072	3.755	5.415	6.882	8.100	9.040
KER 1500/50 phr SiO_2 modified with U-511	1.518	2.492	4.548	6.414	7.890	9.016	–
KER 1500/50 phr SiO_2 modified with U-15	1.536	2.522	4.786	6.814	8.550	–	–
NH_4Cl							
KER 1500/50 phr SiO_2	1.394	2.460	4.120	5.120	–	–	–
Ultrasil VN3							
KER 1500/50 phr Ultrasil VN3	1.250	2.010	3.420	4.805	5.750	6.425	6.620

Table 4 Mechanical properties of the silica-filled vulcanizates studied

Mixture	Tensile strength (MPa)	Elongation at break (%)	Tear strength (kN m^{-1})	Elasticity according to Schob	Hardness (°ShA)
NH_4HCO_3					
KER 1500 unfilled	1.55	352	12.1	52.3	45.1
KER 1500/50 phr SiO_2	7.62	676	38.2	46.9	61.9
KER 1500/50 phr SiO_2 modified with A-189	9.61	669	39.3	47.7	61.8
KER 1500/50 phr SiO_2 modified with U-511	9.74	567	34.5	51.2	59.8
KER 1500/50 phr SiO_2 modified with U-15	10.32	540	36.5	51.5	60.6
NH_4Cl					
KER 1500/50 phr SiO_2	6.00	391	28.8	48.1	61.1
Ultrasil VN3					
KER 1500/50 phr Ultrasil VN3	8.03	650	40.1	47.7	62.0

Table 5 Temperature increments on lower edges of the vulcanizate samples studied

Mixture	Temperature increment at 25 min AT (°C)	Time required to reach thermal equilibrium Tz (min:s)
NH_4HCO_3		
KER 1500 unfilled	5.9	5′30″
KER 1500/50 phr SiO_2	18.1	8′30″
KER 1500/50 phr SiO_2 modified with A-189	21.2	10′
KER 1500/50 phr SiO_2 modified with U-511	18.2	9′30″
KER 1500/50 phr SiO_2 modified with U-15	21.2	10′30″
NH_4Cl		
KER 1500/50 phr SiO_2	15.7	8′30″

Table 6 Vulcanization time (optimum of vulcanization) for samples of studied vulcanizates (temperature 145 °C)

Mixture	Time of vulcanization for t_o(90)
NH_4HCO_3	
KER 1500 unfilled	9′5″
KER 1500/50 phr SiO_2	9′06″
KER 1500/50 phr SiO_2 modified with A-189	9′97″

macromolecules due to interactions of the filler and the rubber. The properties of the filled rubber vulcanizates depend on the degree of filler dispersion to a significant extent.

Results of temperature increments at lower edges of samples surface for all vulcanizates tested are presented in Table 5 (means from two measurements).

The data on the vulcanization kinetics in a rheometer at 145 °C are presented in Table 6.

Upon the mechanical processing and vulcanization, different chemical and physical processes take place between the blend components and, thus, also at the interface between the filler and the basic component, i.e. the rubber. The final strengthening effect reflects complex interaction of the van der Waals forces and formation of chemical bonds. Chemical phenomena developing at the filler/polymer interface reflect chemical reactivity of functional groups present on the filler surface. Introduction of the filler to the blend leads to the reinforcing effect and significantly affects the processing properties of the blend.

Conclusions

Surface modification of the silica precipitated using ammonium hydrogencarbonate or ammonium chloride promotes increase in the silica's capacity to absorb paraffin oil. The silica precipitated using ammonium hydrogencarbonate without addition of a silane agent exhibits a low tendency to form secondary agglomerates, while the silica modified with 3 wt/wt of mercaptosilane demonstrates the presence of exclusively primary agglomerates, with formation of no secondary agglomerates. The silica surface modification using silane coupling agents improves the tensile strength and tear strength of vulcanizates.

The reinforcing effect of the silicas precipitated with the ammonium salts (in particular ammonium hydrogencarbonate) was comparable to that of the silicas commonly used as fillers of synthetic rubber (e.g. Ultrasil VN3).

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