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Surface properties and dispersion behaviour of precipitated silicas

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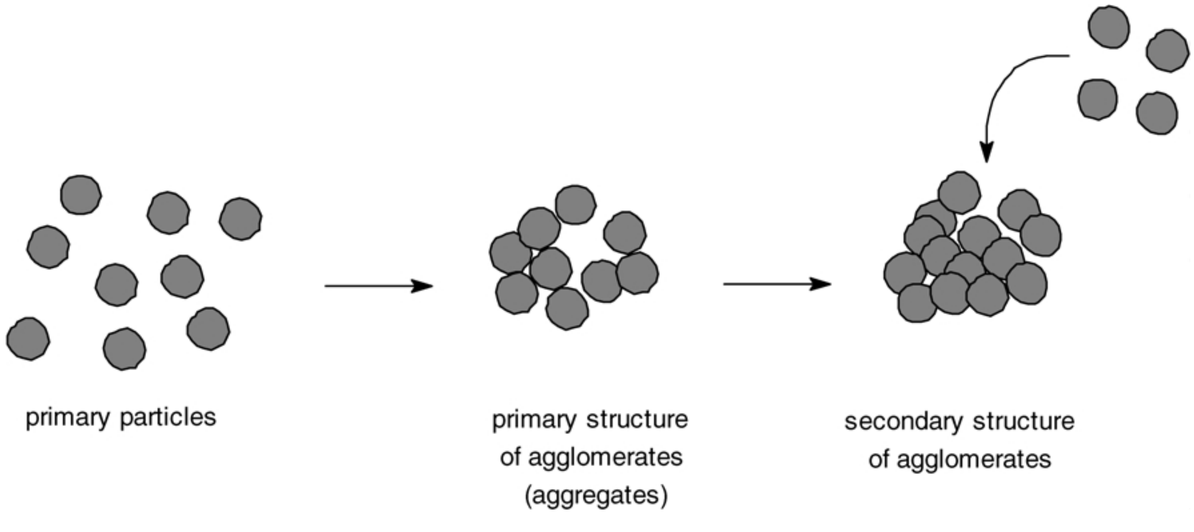
Silicas of highly dispersion degree were obtained using the precipitation technique with sodium metasilicate solution and sulphuric acid. This process includes formation of silica particle and their aggregation. Studies on the surface modification of silicas using silane coupling agents are described. Application of these compounds results in the change of the hydrophilic character to the hydrophobic one. Basic physicochemical analyses of the obtained silica were presented. Moreover, studies on morphology and microstructure using scanning electron microscopy (SEM) were performed. The zeta potential, polydispersity and changes in the tendency to form agglomerates and aggregates of the particles were also described. Silicas modified with any of the examined silanes manifest a decreased tendency to secondary agglomerate formation and in many cases uniform silicas were obtained.

1. Introduction

Silicas exist in multiple forms, which differ between each other both in the chemical and physical respect. They may be crystalline (e.g., quarz) or amorphic (pyrogenic or precipitated silicas) [1–3]. Silicas may be hydrophobic, when their surface groups are represented mainly by siloxane groups (≡Si-O-Si≡) or hydrophilic, when silica surface exposes to action of outer agents silanol groups (≡Si-OH). Presence of the two functional groups affects properties of silica surface and, therefore, modifies their application potential [4].

A hydrophobic silica may be turned into a hydrophilic one by "hydroxylation" of siloxane groups into silanol groups [5]. The reaction is reversible and, thus, a hydrophilic silica may be transformed into a hydrophobic one due to "dehydroxylation", e.g., by heating the surface to >300°C, which transforms silanol groups into siloxane groups. The surface of precipitated silica carries, on the average, 5-6 silanol groups per nm^2 and, therefore, it exhibits a hydrophilic character while siloxane groups remain non-reactive. The active silanol groups at the silica surface are responsible for formation of particle aggregates and agglomerates [6]. Primary particles of silica become coupled to each other by hydrogen bonds at first into primary agglomerates (aggregates) which, at a further stage, bind forming spatial structures of secondary agglomerates. The tendency of hydrated silica particles to form aggregates and agglomerates is illustrated schematically:



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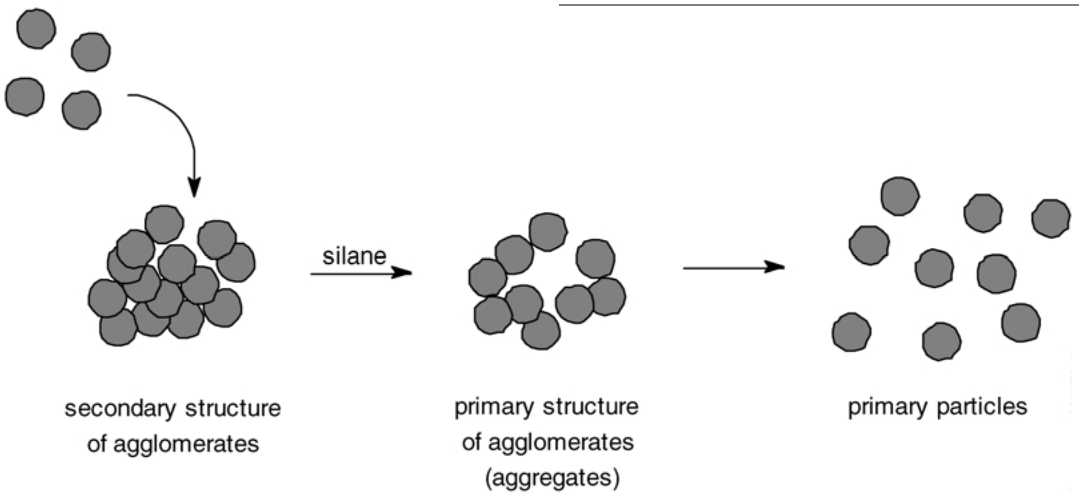
Reactivity of silanol groups allows for chemical modification of silica surface [7–17]. In the course of the process, silanol groups react with substituents of the modifying compounds which leads to a decrease in the amount of the former. This induces decomposition of agglomerates into aggregates and appearance of primary particles in the systems of modified silicas:



Reactions of silica surface silanol groups with organic compounds lowers or ablates hydrophilic properties of silica and promotes appearance at the silica surface of novel organofunctional groups with high affinity to organic compounds. Due to the presence of silanol groups, surface of precipitated silicas reacts chemically with silanes (e.g., with silane coupling agents), metal and non-metal halides, alcohols, surfactants, etc. Considering all transformations on SiO_2 surface, electron structure and properties of ≡Si-OH bonds, the processes may be regarded to represent nucleophilic and electrophilic substitution [18].

The surface-adsorbed compounds induce the earlier mentioned surface hydrophobization while filler surfaces acquire in this way an organophilic character, i.e., their chemical affinity increases to functional groups of polymers (rubbers, polyurethanes, etc.) [19] as well as to hydrophobic media in paints and varnishes [16, 17].

2. Experimental details

2.1. Materials

Highly dispersed silicas were obtained in the process of precipitation from aqueous solutions of sodium metasilicate ($Na_2O * mSiO_2 * nH_2O$) using sulphuric acid in presence of: hydrophobicity-inducing agent—Rokanol K-7 ($C_{18}H_{37}O(CH_2CH_2O)_7H$) and coagulating agent—sodium sulphate(VI). Silane proadhesive compounds (from the group of silane coupling agents) presented in Table I were used as agents which modified the precipitation system.

2.2. Preparation and modification of hydrated silicas

Sodium metasilicate solution, containing appropriate amount of the coagulating agent (sodium sulphate(VI)), and 5 wt% solution of sulphuric acid were dosed in parallel to a reactor of 0.5 dm^3 in capacity, containing aqueous solution of the hydrophobicity-inducing agent

TABLE I Principal modifying agents

Symbol	Name of the compound and it formula	Properties
U-511	3-methacryloxypropyltrimethoxysilane $CH_2{=}C(CH_3)COO(CH_2)_3Si(OCH_3)_3$	Molecular weight: 248.0 Boiling temp.(°C): 78-81 Density(g/cm^3): 1.04 Refraction coeff.: n_{D25} – 1.429 Ignition temp.(°C): 92
U-613	vinyltris(2-methoxyethoxy)silane $CH_2{=}CHSi(OCH_2CH_2OCH_3)_3$	Molecular weight: 280.4 Boiling temp.(°C): 133 Density(g/cm^3): 1.04 Refraction coeff.: n_{D25} –1.430 Ignition temp.(°C): 56
U-187	3-glycydoxypropyltrimethoxysilane $(OCH_2CH)CH_2O(CH_2)_3Si(OCH_3)_3$	Molecular weight: 276.5 Boiling temp.(°C): 290 Density(g/cm^3): 1.06 Refraction coeff.: n_{D25} –1.427 Ignition temp.(°C): 135
A-189	3-mercaptopropyltrimethoxysilane $HS(CH_2)_3Si(OCH_3)_3$	Molecular weight: 224.0 Boiling temp.(°C): 106 Density(g/cm^3): 0.985 Refraction coeff.: n_{D25} – 1.43

U—UniSil, A—Witco.

TABLE II Physicochemical parameters of silicas obtained in sodium metasilicate and sulphuric acid solution in presence of coagulant—Na_2SO_4 and Rokanol K-7

Sample no.	Water absorbing capacity (cm^3/100 g)	Dibutyl phthalate absorbing capacity (cm^3/100 g)	Paraffin oil absorbing capacity (cm^3/100 g)	Bulk density (g/dm^3)
1	400	650	1200	91
2	350	550	900	121
3	350	550	850	136
4	400	650	1100	104
5	550	800	1250	74
6	550	750	1200	82
7	450	725	1150	85
8	500	750	1150	91
9	500	700	1200	89

(0.25 weight parts of Rokanol K-7 per 100 weight parts of SiO_2). The system was intensely blended using a propeller top stirrer. A thermostate allowed to maintain steady temperature of 85°C. The precipitation process was conducted until pH of the mixture stabilized at the level of 5 to 7. The reaction yielded a white silica powder, which was washed with water, filtered and dessicated in a stationary drier for 48 h at 105°C.

The method of silica precipitation significantly affected physicochemical parameters of silica. Specificity of the process involved strict control of the amounts of dosed solutions and appropriate timing of adding them to the reactor. The data presented in Table II allowed to select sample 5, which showed optimum physicochemical properties.

Modification of silica surface was conducted by adding appropriate proadhesive compound to the reactive mixture. Products of the best physicochemical properties were obtained when the modifier was applied at the terminal stage of precipitation. The optimum duration of modification in the course of precipitation of the hydrated silica amounted to 20 min. Similarly to the silica precipitation process with no parallel modification, the obtained product was subjected to further processing.

The modification process was conducted basing on the earlier established optimum parameters of silica precipitation. We have found technologically proper to modify highly dispersed silica obtained in the medium of Rokanol K-7 and sodium sulphate(VI). Silane coupling agents, applied at the amounts of 1, 2, 3, 5, or 10 weight parts per 100 weight parts of SiO_2 were used to modify the precipitation system.

2.3. Physicochemical properties of the obtained silicas

Following the precipitation, the silicas were subjected to physicochemical tests, their bulk densities as well as water, dibutyl phthalate and paraffin oil absorbing capacities were estimated.

Studies on morphology and microstructure were performed in order to obtain data on dispersion, particle shape and morphology of the granules, structure of individual particles and on silica aggregation and agglomeration type following precipitation. The studies were conducted using scanning electron microscopy (SEM). The observation were performed in the Phillips SEM 515 microscope.

Laser Doppler electrophoretic light scattering determinations were performed with a ZetaPlus instrument (Brookhaven Instruments Inc., USA), in the reference beam mode at the wavelength of laser light source of 635 nm, sampling time 256 μs, modular frequency 250 Hz and the scattering angle 15°. The standard error of the zeta potentials, converted from the experimentally determined electrophoretic mobilities according to the Smoluchowski limit of the Henry equation, was typically $<1.0\%$. The zeta potentials were obtained by averring 5–10 runs.

Size distribution of silica particle agglomerates and aggregates were also estimated using a ZetaPlus instrument by dynamic light scaterring method. In the instrument, the mobility rate is measured of loaded colloid particles, suspensed in a water.

Specific surface areas of silica powders were determined by N_2 adsorption (BET method) using ASAP 2010 instrument (Micrometrics Instrument Corporation). Moreover, the volume and size of pores of precipitated materials were examined. Samples were heated at 120°C for 2 hours prior to measurements.

3. Results and discussion

The studies performed on the process of precipitation of highly dispersed silicas in the medium of organic compounds permitted to establish optimum parameters of conducting the process.

Aqueous solution of the non-ionic surfactant, Rokanol K-7 was used as a hydrophobicity-inducing compound. The agent was supposed to restrict the number of silanol groups formed on the silica surface. This justified its name of a hydrophobicity-inducing compound.

Moreover, in the course of the studies a significant effect was disclosed of the concentration of the coagulating agent on a form of precipitated silica and on quality of the final product. The optimum conditions were found to involve precipitation in the presence of 2.5 wt% sodium sulphate(VI) in the solution of sodium metasilicate.

In this way, parameters were establish for production of silica which exhibited optimum dispersion and appropriate development of the outer surface. The silicas were obtained at the following parameters of the process: temperature of 85°C, silicate modulus of sodium metasilicate solution of 3.3, starting concentration of sodium metasilicate solution of 5 wt%, concentration of sulphuric acid of 5 wt%, rate of dosing sodium metasilicate solution of 2.2 cm^3/min, rate of dosing sulphuric acid of 0.23 cm^3/min and final pH of the mixture of 5.

Effects of the type and amount of silane coupling agents carrying various groups (vinyl-, glycidoxy- and mercapto- groups) on bulk density of the silica and the capacity to absorb water by the silica are presented in Figs 1 and 2.

The compounds induced change in properties of the precipitated silica. Silica surface modification performed in the course of the precipitation process exerted a significant effect on values of its bulk density. Silicas

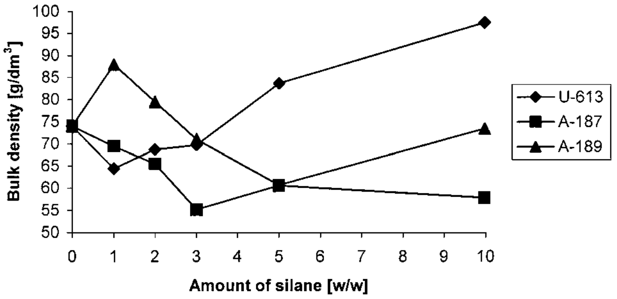


Figure 1 Effect of amounts of modifying agent on the bulk density of silicas.

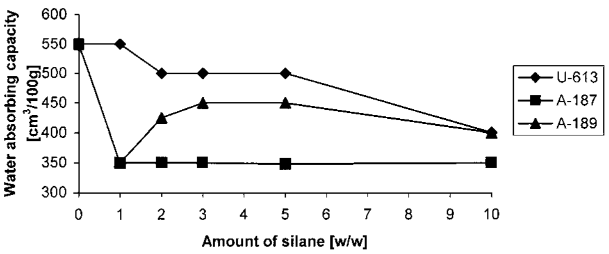


Figure 2 Effect of amounts of modifying agent on the water absorbing capacity of silicas.

of a low bulk density are particularly looked for. Such silicas were obtained upon modification with the use of glycidoxysilane (A-187), which yielded silicas of very low bulk densities.

Similar values of bulk densities were typical for silicas formed during modification with mercaptosilane (A-189). On the other hand, application of vinylsilane (U-613) resulted in augmented bulk densities (in particular following modification with 5 or 10 weight parts of the silane/100 weight parts of silica).

Silicas modified with U-613, A-187 or A-189 silanes exhibited significantly lower values of water absorption than that shown by the original, unmodified silica (sample 5). A particularly low capacity to absorb water was noted following modification using glycidoxysilane: the capacity to absorb water decreased from 550 cm^3 for the original silica to 350 cm^3 per 100 g of modified silica. Application of mercapto- or vinylsilane for the modification was also followed by a decrease in the water absorbing capacity but only to 400 cm^3/100 g.

Values of zeta potential, electrophoretic mobility and polydispersity for the unmodified silica and for silicas modified with silane coupling agents are given in Table III.

The original silica showed a highly stable dispersion. Its electrokinetic potential (zeta potential) amounted to (−20.85) mV. Following silane modification, the silicas exhibited a similar character of the surface charge and showed zeta potential values ranging between (−15.58) and (−27.44) mV.

The precipitated hydrated silica manifested the polydispersity level of 0.160. On the other hand, the silicas modified with silane coupling agents showed an almost twofold higher polydispersity. This probably resulted from changes in aggregate-adhesion system of the formed silica dispersion.

TABLE III Zeta potential, electrophoretic mobility nad polydispersity of unmodified and modified precipitated silicas

Sample no.	Amount of silane (w/w)	Zeta potential (mV)	Electrophoretic mobility ((m/s) / (V/cm))	Polydispersity
		No silane		
5	–	−20.85	−1.63	0.160
		U-613		
15	1	−16.99	−1.33	0.273
17	3	−24.81	−1.94	0.258
18	5	−18.54	−1.45	0.298
19	10	−24.34	−1.90	0.280
		A-189		
20	1	−21.22	−1.66	0.205
22	3	−25.98	−2.03	0.222
23	5	−23.65	−1.85	0.219
24	10	−19.88	−1.55	0.245
		A-187		
40	1	−15.58	−1.22	0.310
42	3	−24.70	−1.93	0.228
43	5	−27.44	−2.14	0.185
44	10	−22.39	−1.75	0.289
		U-511		
13	5	−18.23	−1.42	0.292

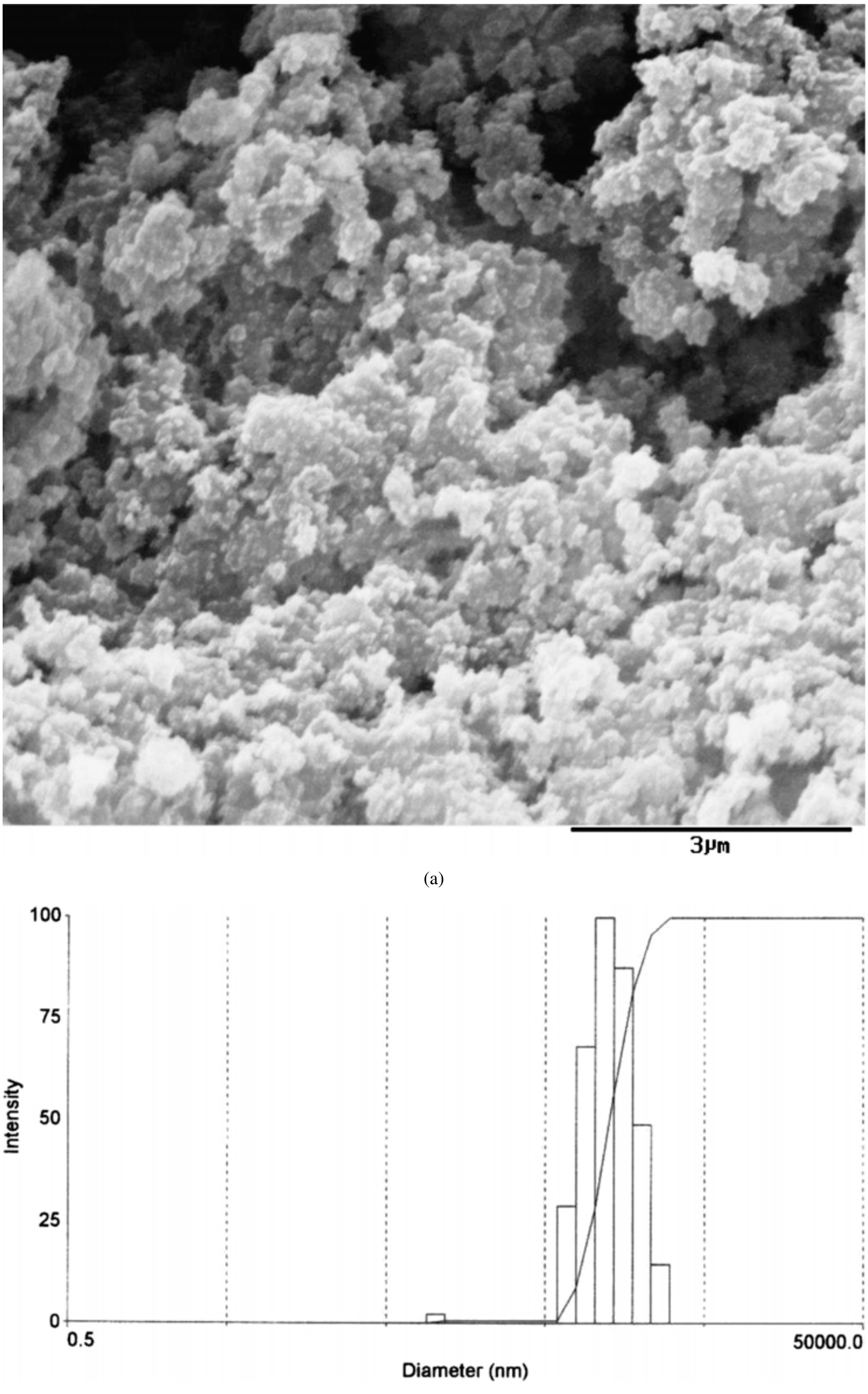
TABLE IV Particles effective diameter and mean size of aggregates and agglomerates of unmodified and modified precipitated silicas

Sample no.	Amount of silane (w/w)	Effective diameter (nm)	Mean size of aggregates[a] (nm)	Mean size of agglomerates[a] (nm)
			No silane	
5	–	1140.3	100.9/2	1161.7/100
			U-613	
15	1	583.3	183.1/28 : 286.2/74	1182.8/100
17	3	289.0	–	489.2/100
18	5	678.1	110.0/9 : 426.8/84	1464.4/100
19	10	898.0	98.6/4 : 471.0/53	1569.1/100
			A-189	
20	1	223.3	155.2 : 498.3/60	–
22	3	307.1	130.0/24 : 330.0	2902.4/17
23	5	255.7	–	365.0/100
24	10	898.0	98.6/4 : 471.0/53	1569.1/100
			A-187	
40	1	635.1	153.2/39 : 607.3	2406.8/95
42	3	253.6	176.8 : 597.5/81	–
43	5	233.4	156.1/59 : 410.8/100	–
44	10	898.0	98.6/4 : 471.0/53	1569.1/100
			U-511	
13	5	598.2	130.9/19 : 484.0	2324.2/74

[a]Max. intensity of aggregates—100 and max. intensity of agglomerates is presented in table.

Data on the effective particle diameter and on mean sizes of particle aggregates and agglomerates for unmodified silicas and for silicas modified with U-613 vinylsilane, A-189 mercaptosilane, A-187 glycidoxysilane and U-511 metacryloxysilane are presented in Table IV. Size distributions of respective particle aggregates and agglomerates as well as electron micrograph of silica precipitated in the medium of Rokanol K-7 and sodium sulphate (VI) with no modification are presented in Fig. 3.

Silica precipitated in the absence of silane agent exhibited a very high tendency to form secondary agglomerates. The agglomerates involved vast volumes, consisting of primary agglomerates (aggregates)



(a)

(b)

Figure 3 SEM (a) and particle size distribution (b) of unmodified silica.

of the particles. This was confirmed by electron microscopic patterns of the unmodified silica (Fig. 3a), presenting giant particle agglomerates. Particle size distribution curve for the unmodified silica (Fig. 3b) manifested the very evident broad band within the range of 675–2622 nm (maximum intensity of 100 corresponded to agglomerate diameter of 1161.7 nm). The band was typical for secondary agglomerates of precipitated hydrated silicas (the silica showed a very high the water absorbing capacity: 550 cm^3/100 g). Effective diameter of unmodified silica particles amounted to 1140.3 nm.

Particle size distributions and electron micrograph of precipitated silicas, modified with various amounts of vinylsilane, are presented in Figs 4–6.

Following modification of silica surface with 1 weight part of vinylsilane a moderate tendency for formation of secondary agglomerates was observed, as well as low homogeneity and presence of three bands

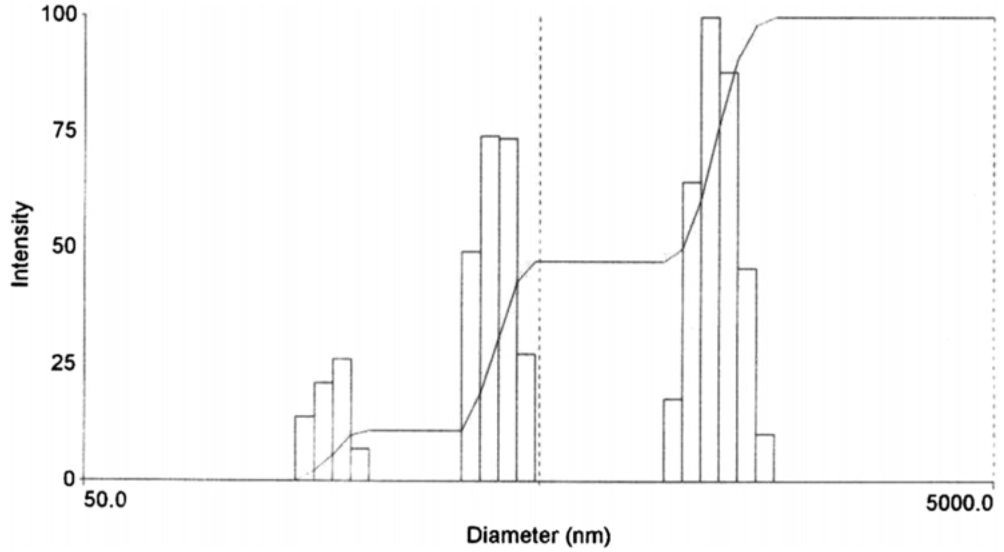


Figure 4 Particle size distribution of modified silica with 1 weight part of U-613 silane.

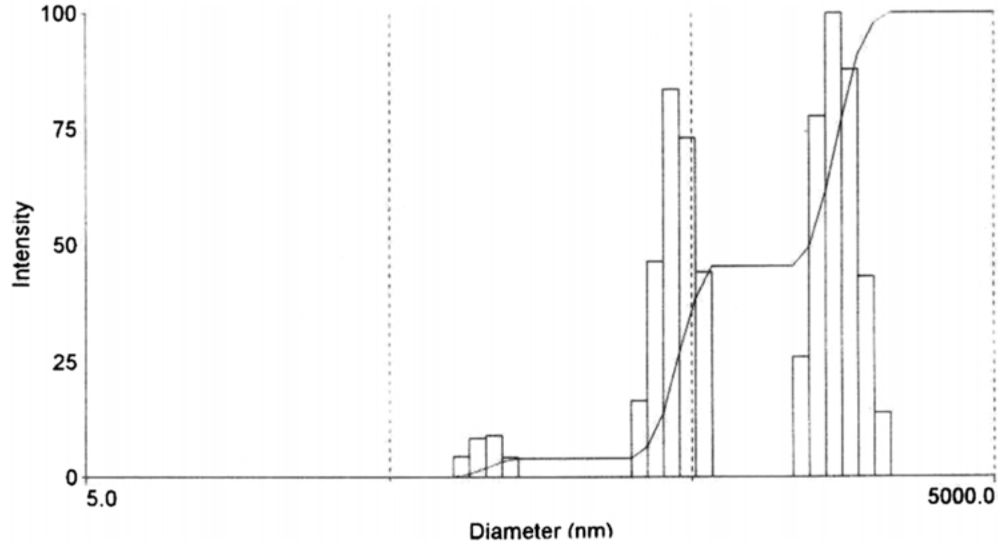
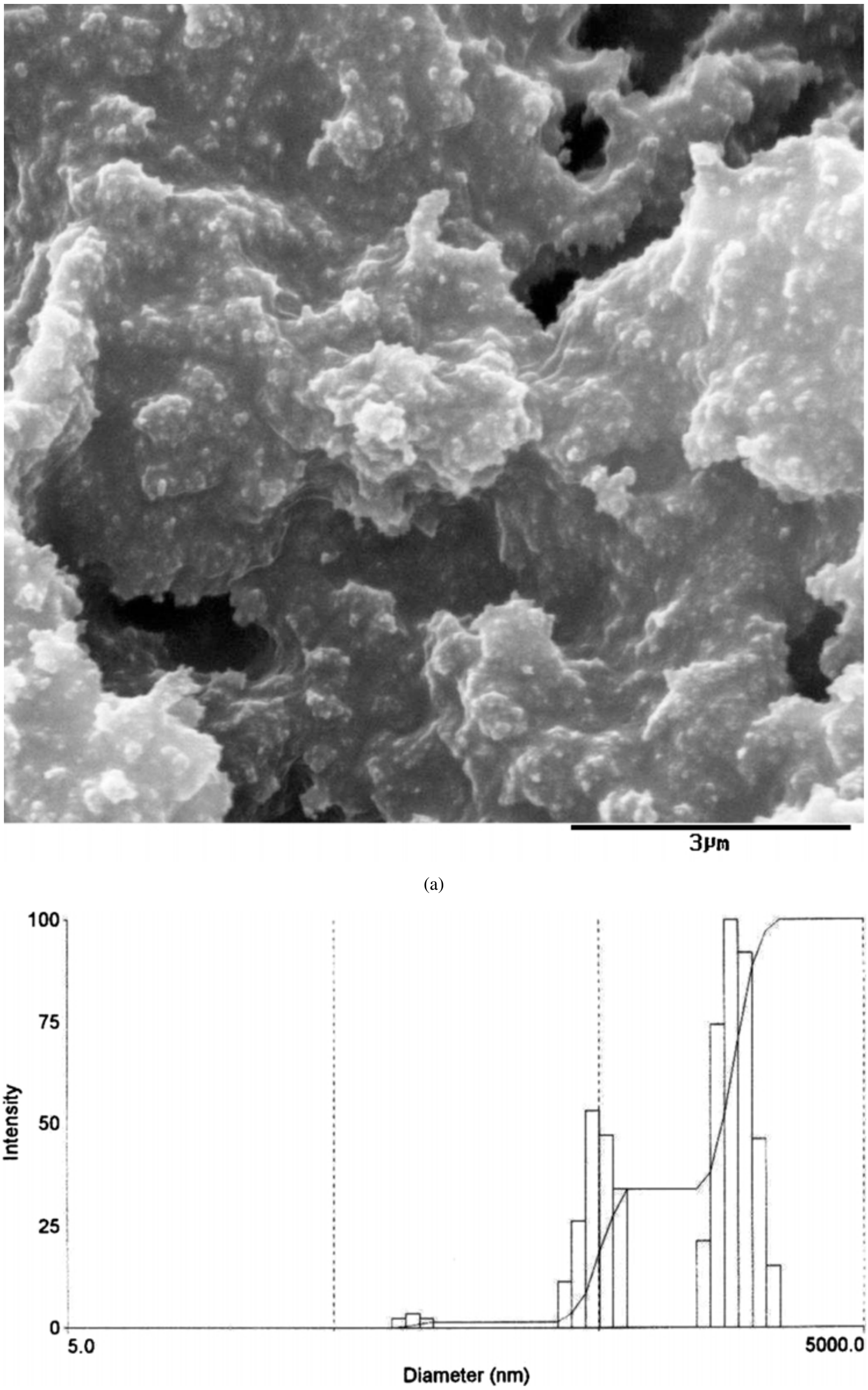


Figure 5 Particle size distribution of modified silica with 5 weight parts of U-613 silane.

of agglomerates of various diameters (Fig. 4). Effective diameter of the agglomerates was 583.3 nm. Two bands of primary agglomerates were noted within the range of very small diameters: the less intense within the range of 150–200 nm (maximum intensity of 28 corresponded to agglomerate diameter of 183.1 nm) and the other within the diameter range of 350–465 nm (maximum intensity of 74 corresponded to the agglomerate diameter of 286.2 nm). At the limit of secondary agglomerate manifestation an intense band was seen within the range of 980–1425 nm (maximum intensity of 100 corresponded to the agglomerate diameter of 1182.8 nm).

Increase in the amount of vinylsilane present in the course of silica surface modification (to more than 5 weight parts) exerted negative effect on agglomerate structure of the silica, resulting in a markedly increased tendency to form secondary agglomerate structures. Following modification with 5 weight parts of vinylsilane, effective diameter of the agglomerates increased to 678.1 nm, from 583.3 nm following modification with one weight part of the silane. Moreover, the agglomerate bands tended to manifest higher diameters (Fig. 5). In the range of primary agglomerates of low diameters a very low intensity band of 85–125 nm was observed (maximum intensity of 9 corresponded to the diameter of 110 nm) and a more intense band within the range of agglomerate diameters of 330–550 nm (maximum intensity of 84 corresponded to the agglomerate diameter of 426.8 nm). A very intense band was also observed at the limit of secondary agglomerates, within the range of 1140–2200 nm (maximum intensity of 100 corresponded to the secondary agglomerate diameter of 1464.4 nm).

A further increase in the amount of vinylsilane used for the modification (up to 10 weight parts) resulted in even more accentuated silica particle agglomeration. The change was confirmed, first of all, by SEM microphotographs of the silica following modification with 10 weight parts of vinylsilane (Fig. 6a). As demonstrated by the curve of particle size distribution for the silica modified with 10 weight parts of the silane U-613 (Fig. 6b), the so treated sample contained significantly more secondary agglomerates within the



(a)

(b)

Figure 6 SEM (a) and particle size distribution (b) of modified silica with 10 weight parts of U-613 silane.

range of 1230–2250 nm (maximum intensity of 100 corresponded to a secondary agglomerate diameter of 1569.1 nm). Effective agglomerate diameter evidently increased to 898.0 nm. Primary agglomerates were relatively infrequent and formed two low intensity bands: one within the range of 80–115 nm (maximum intensity of 4 corresponded to the agglomerate diameter of 98.6 nm) and the other within the range of 370–600 nm (maximum intensity of 53 corresponded to the agglomerate diameter of 471 nm). The results proved that application of more than 5 weight parts of silane for the silica modification was pointless and inadvisable, as it led to deteriorated properties of the silica.

Silicas modified with mercaptosilane (A-189) manifested low tendency to form agglomerates, practically until 1–3 weight parts of the silane were used for their modification. In the curve of particle size distribution for silica modified with one weight part of

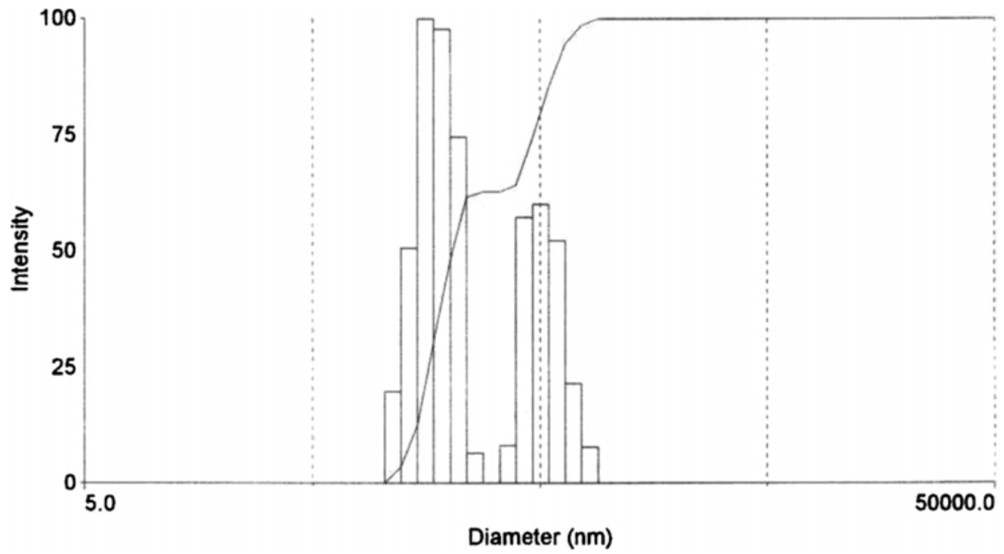
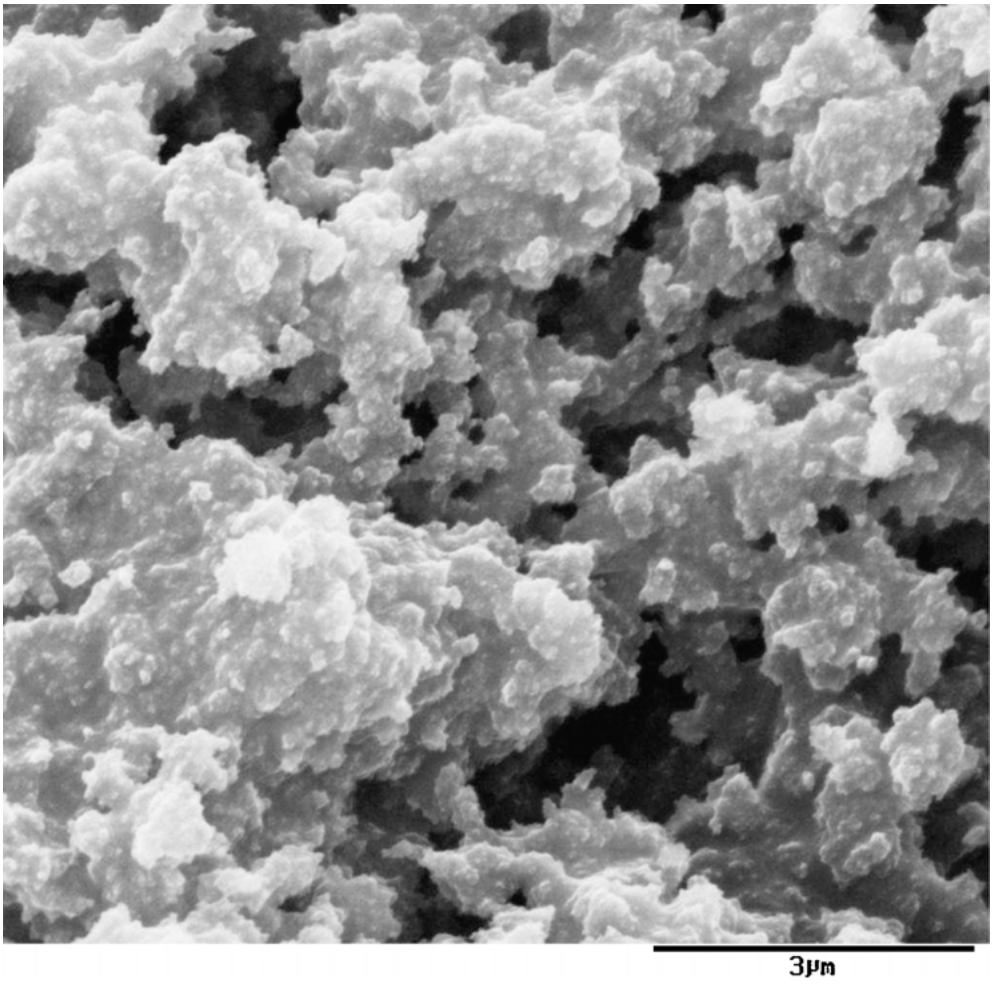


Figure 7 Particle size distribution of modified silica with 1 weight part of A-189 silane.

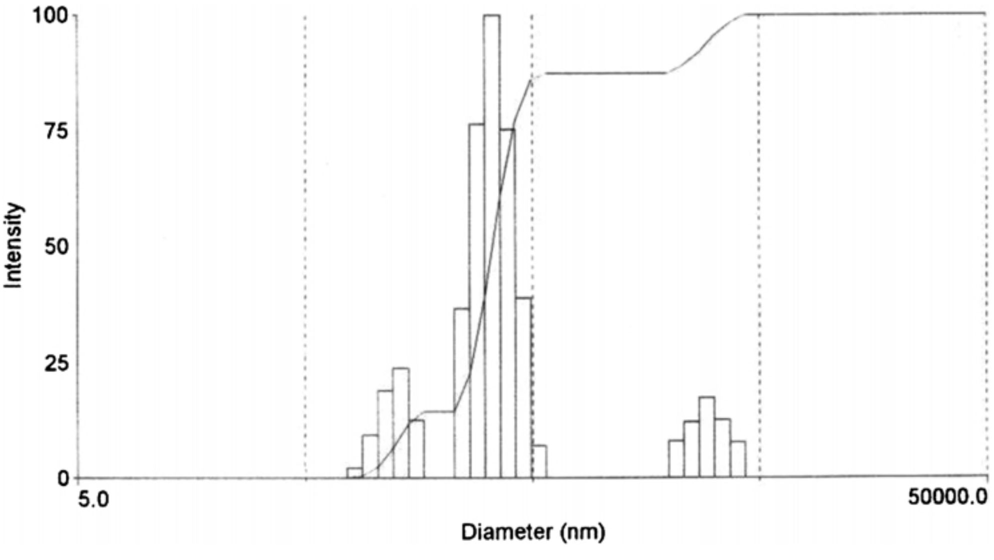
mercaptosilane (Fig. 7) two bands could be distinguished, corresponding to primary agglomerates (aggregates), including one of a very high intensity within the range of 110–300 nm (maximum intensity of 100 corresponded to the aggregate diameter of 155.2 nm) and another one of a lower intensity within the range of 350–820 nm (maximum intensity of 60 corresponded to the diameter of primary agglomerates of 498.3 nm). Silica precipitated in such conditions exhibited a highly uniform character while effective diameter of its particles amounted to 223.3 nm.

Silica precipitated in the presence of 3 weight parts of mercaptosilane exhibited an already less uniform character and higher effective particle diameter of 307.1 nm.



(a)

Figure 8 SEM (a) and particle size distribution (b) of modified silica with 3 weight parts of A-189 silane. (*Continued*).



(b)

Figure 8 (*Continued*).

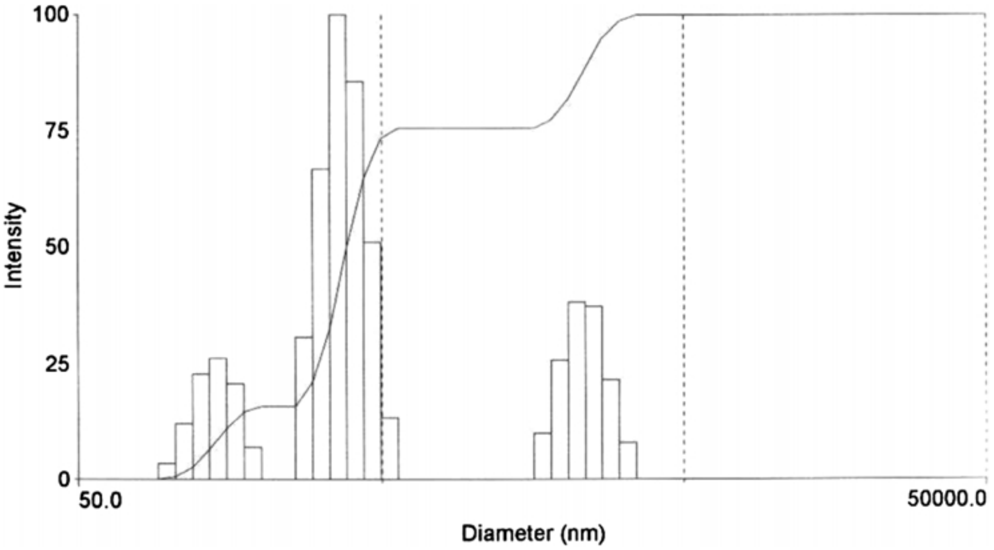
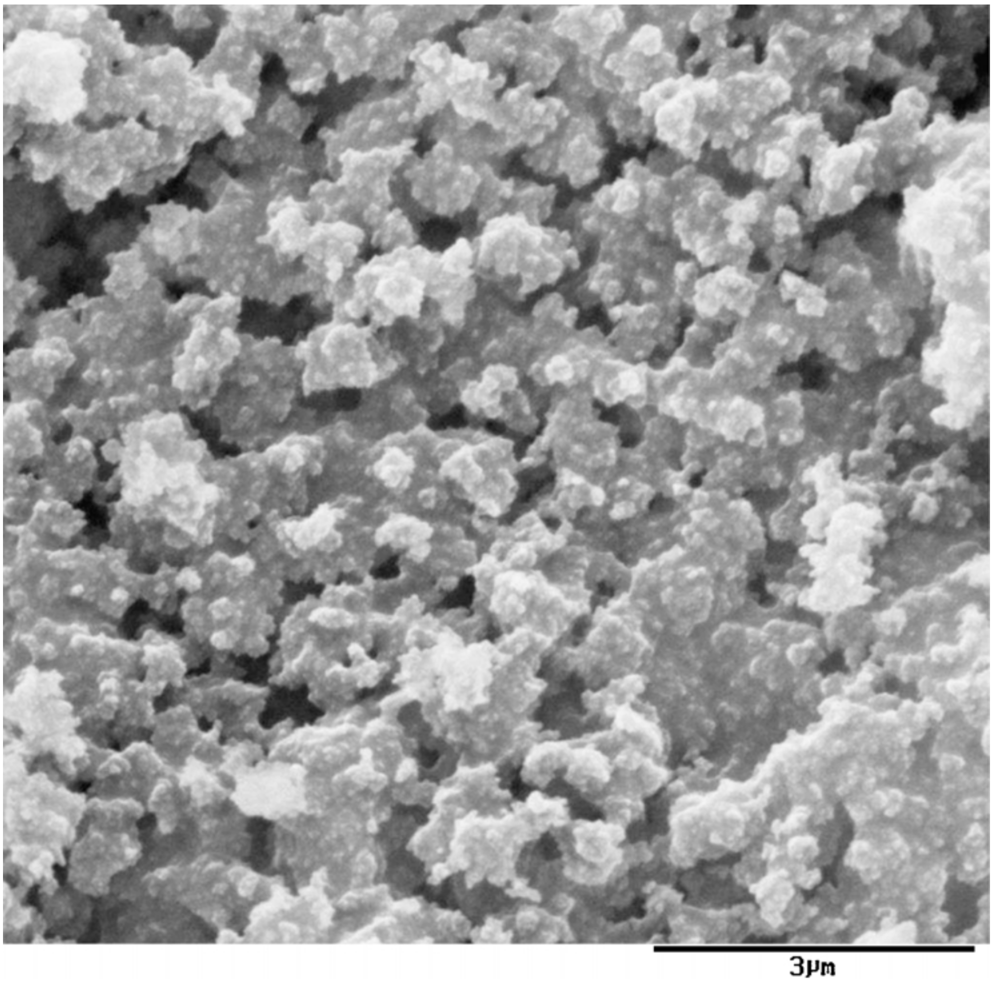


Figure 9 Particle size distribution of modified silica with 10 weight parts of A-189 silane.

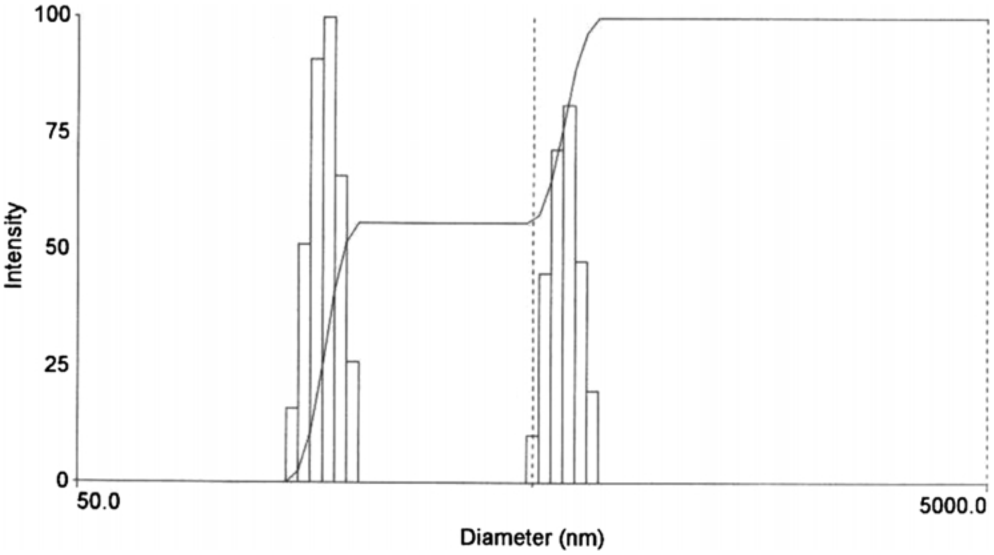
This was confirmed by the data of Fig. 8a and b: particle size distribution for the silica modified with 3 weight parts of the silane A-189 (Fig. 8b) proved that the silica structure contained few secondary agglomerates within the range of 2100–4000 nm (maximum intensity of 17 corresponded to the diameter of secondary agglomerates of 2902.4 nm). The agglomerate structure of silica precipitated in the presence of 3 weight parts of mercaptosilane included first of all primary agglomerates, present within two ranges: the less intense band of the agglomerates of lower diamaters within the range of 80–155 nm (maximum intensity of 24 corresponded to the agglomerate diameter of 130 nm) and the other, very intense band within the range of 240–550 nm (maximum intensity of 100 corresponded to the agglomerate diameter of 330 nm).

Following modification with 10 weight parts of mercaptosilane, silica was even less uniform and exhibited an even higher tendency to form secondary agglomerates. The effective agglomerate diameter was 388.1 nm. In the curve of particle size distribution (Fig. 9) three bands could be distinguished: two bands ascribed to the presence of primary agglomerates and one reflecting presence of secondary agglomerates. Primary agglomerates were present within the range of 90–190 nm (maximum intensity of 26 corresponded to the agglomerate diameter of 143.7 nm) and within the range of 275–530 nm (maximum intensity of 100 corresponded to the agglomerate diameter of 356.7 nm). Secondary agglomerates formed large accumulations of diameters ranging from 1700 to 3200 nm (maximum intensity of 38 corresponded to the diameter of secondary agglomerates of 2196.0 nm).

Particle size distributions and electron micrographs of silicas modified with glycidoxysilane A-187, at various amounts of the silane used for modification, are shown in Figs 10 and 11. Particularly advantageous results were obtained for silica samples modified with 3 and 5 weight parts of glycidoxysilane. The electron micrographs documented a complete absence of secondary agglomerates (Figs 10a and 11a). Following modification with 3 weight parts of A-187 silane,



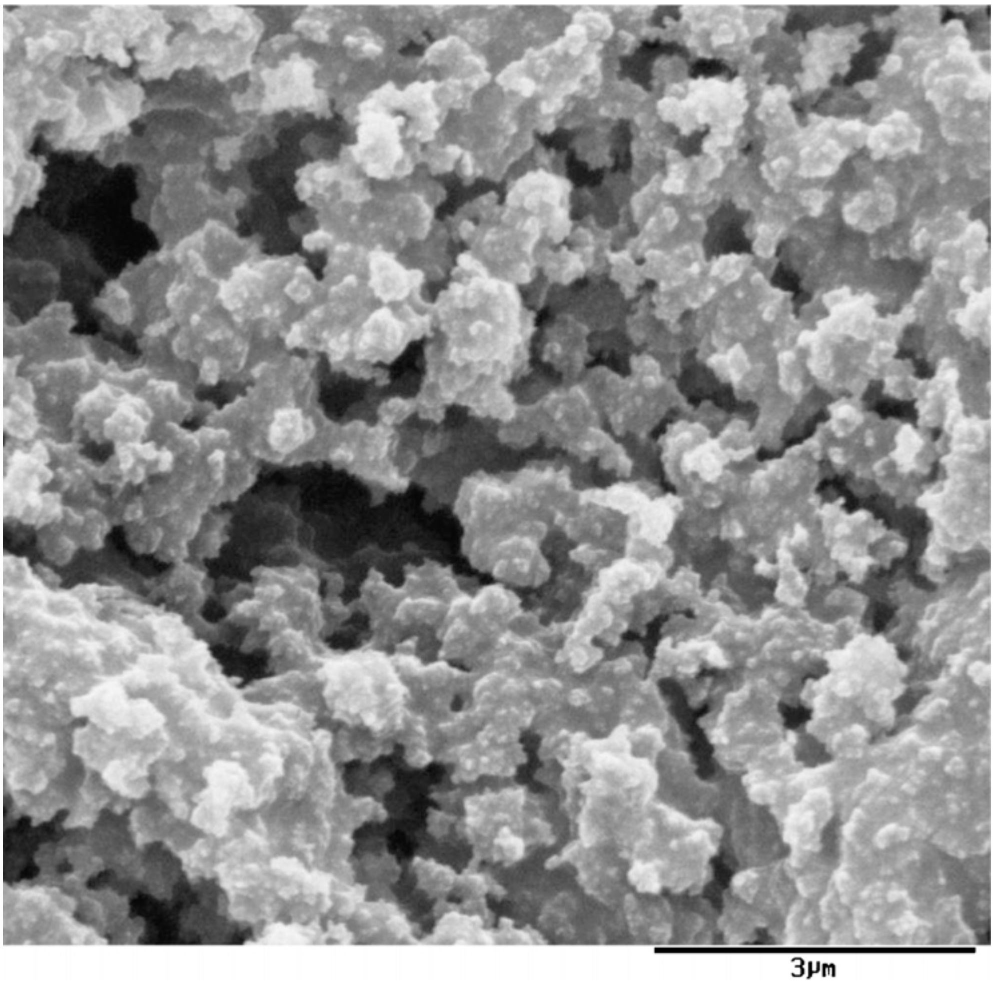
(a)



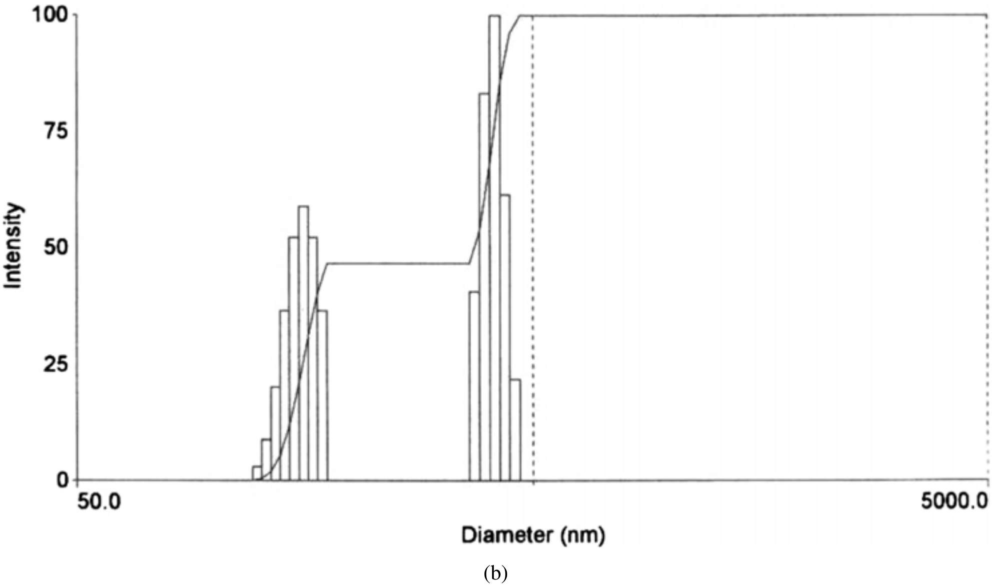
(b)

Figure 10 SEM (a) and particle size distribution (b) of modified silica with 3 weight parts of A-187 silane.

the particle size distribution curve (Fig. 10b) manifested two bands, ascribed to the presence of primary agglomerates: the more intense one within the range of 145–200 nm (maximum intensity of 100 corresponded to the diameter of 176.8 nm) and the low intensity band within the range of 500–675 nm (maximum intensity of 81 corresponded to the agglomerate diameter of 597.5 nm). The effective particle diameter was 253.6 nm. Following modification with 5 weight parts of glycidoxysilane, the silica manifested an even lower effective agglomerate diameter of 233.4 nm. Microscope studies confirmed the low tendency to form secondary agglomerates (Fig. 11a). The particle size distribution curve (Fig. 11b) demonstrated two bands,



(a)

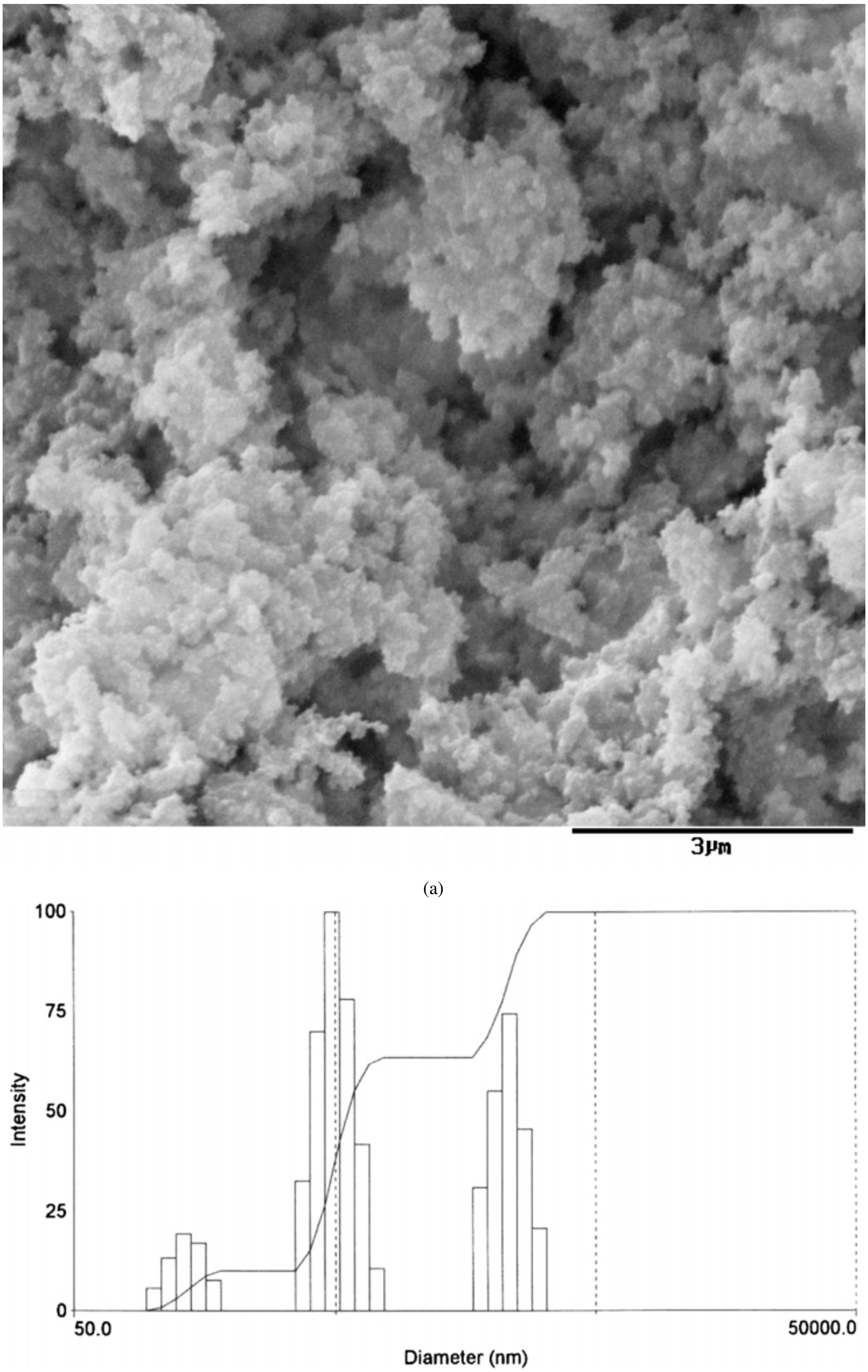


(b)

Figure 11 SEM (a) and particle size distribution (b) of modified silica with 5 weight parts of A-187 silane.

related to presence of primary agglomerates of the silica. Both bands represented low diameters of the agglomerates: the one of lower intensity fitted the range of 130–170 nm (maximum intensity of 59 corresponded to the agglomerate diameter of 156.1 nm) and the other of high intensity, corresponding to the range of 370–455 nm (maximum intensity of 100 corresponded to the agglomerate diameter of 410.8 nm).

Following modification of silica with 5 weight parts of metacryloxysilane, a tendency for decomposition of secondary agglomerates was observed but the silica became less uniform (Fig. 12). The curve of particle size distribution manifested three bands of a very different intensity. The effective agglomerate diameter decreased markedly to 598.2 nm. As shown in Fig. 12b, two bands characterized presence of the so called primary



(a)

(b)

Figure 12 SEM (a) and particle size distribution (b) of modified silica with 5 weight parts of U-511 silane.

agglomerates (aggregates). Each of the bands showed a distinct intensity. Most numerous were primary agglomerates within the range of 370–720 nm (maximum intensity of 100 corresponded to the agglomerate diameter of 484.0 nm). A band of lower intensity was also present, representing agglomerates of lower diameters, approximately 100–170 nm (maximum intensity of 19 corresponded to the agglomerate diameter of 130.9 nm). Presence of agglomerates within the latter range was particularly desired as it immensely affected quality of the highly dispersed sediments. Unfortunately, even this silica preparation contained certain proportion of secondary agglomerates, within the range of 1700–3000 nm (maximum intensity of 74 corresponded to the secondary agglomerate diameter of 2324.2 nm).

TABLE V Specific surface area, volume and average size of pores of obtained silicas (evaporated in 120°C)

Sample no.	Specific surface area BET (m^2/g)	Total pores volume (cm^3/g)	Pores volume 8.5 to 1500 Å (cm^3/g) From adsorption curve	Pores volume 8.5 to 1500 Å (cm^3/g) From desorption curve	Average size of pores[a] (Å)
			No silane		
5	137.3	0.3396	0.6434	0.6481	98.9
			U-613		
18	173.7	0.4406	0.8370	0.8406	101.4
			A-187		
43	131.8	0.2609	0.4351	0.4343	79.1

[a]Calculated from BET equation (4V/A).

Values of specific area (BET), volume and size of pores for selected precipitated silicas are shown in Table V. As demonstrated by the data of the table, the unmodified precipitated silica presented highly developed area (137 m^2/g). Modification of the silica using 5 weight parts of U-613 vinylsilane resulted in an even higher specific area (173.7 m^2/g). Silica modified with glycidoxysilane (5 weight parts/100 weight parts of SiO_2) exhibited an almost identical area development to that manifested by the unmodified silica. The two silicas exhibited also a similar pore volume and their average diameter. Silica modified with vinylsilane (sample 18) demonstrated a slightly greater pore diameter (around 101 Å) and a pore volume higher by one order of magnitude (0.4406 cm^2/g) as compared to the original silica and to silica modified with A-187 silane.

4. Conclusions

- Silica precipitated in the absence of silane surface modifiers exhibits strong tendency to form secondary agglomerates. This reflects highly hydrophilic character of its surface. The secondary agglomerate structures can be observed in electron micrographs.
- All precipitated modified and unmodified silicas show similar values of zeta potential (in the range of (−15)–(−30) mV) and of polydispersity (0.100–0.300).
- Silicas modified with any of the examined silanes manifest a decreased tendency to secondary agglomerate formation and in many cases highly uniform silicas are obtained. Agglomerate size distribution curves for such silicas demonstrate presence of primary agglomerates and, in some cases, also of primary particles.
- Specific area of unmodified and modified silicas proves that they represent active fillers. High values of specific area reflect structure and morphology of their surface (they exhibit mainly a macroporous form).

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