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Sol-Gel-Derived Silicon-Containing Hybrids

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Additional information is available at the end of the chapter

<http://dx.doi.org/10.5772/67824>

Abstract

Silicone-containing hybrid systems including functionalized and modified silica nanospheres as well as silica aerogels were synthesized using sol-gel process. The most important advantage of the developed silicon-containing hybrids lies in their high application potential, e.g. for the production of façade paints, polymer nanocomposites, highly efficient insulating materials and other high-tech products for construction industry. The possibility of precise steering of sol-gel process and synergism of very rich silicon compound chemistry allows to obtain materials with strategically designed architecture. Original methods of manufacturing following silicon-containing hybrids such as functionalized and non-functionalized silica nanospheres, silica nanospheres containing immobilized silver and/or copper nanoparticles and silica aerogels were developed. Homogeneous structural properties of synthesized materials were achieved due to carefully selected parameters of sol-gel process. The technology offers a possibility to control the grain size and uniformity of nanospheres by process parameters. The smallest nanosphere size is 10 nm and the largest 600 nm. The properties of aerogels obtained according to the original technology developed in the Industrial Chemistry Research Institute (ICRI) are extremely good and repetitive particularly taking into account their thermal conductivity. The main advantages of the developed aerogels are very good mechanical properties, very low dust formation and significantly decreased costs when compared to traditional silica aerogels.

Keywords: silicon-containing hybrids, silica nanospheres, aerogels

1. Introduction

Synergism resulting from the possibilities of precise steering of sol-gel process and very rich silicon compound chemistry allows to obtain silicon-containing hybrids, especially spherical

nanosilica and aerogels with strategically designed architecture. The key factor in the chemistry of sol-gel process is the complex equilibrium state, which should be achieved for the simultaneous reactions of hydrolysis and condensation according to the following reaction schemes (see **Figure 1**).

A number of parameters affect the sol-gel process [1]. The most important are the ratio of alkoxysilane precursors to water, reaction mixture pH and temperature and mixing speed and time. The successful control of this process needs a lot of practical experience as well as the knowledge of the correlation of the influence of particular factors. Careful adjustment of reaction condition and substrate ratio in sol-gel process allows to obtain several kinds of materials with different physical properties and structures. The structural properties are strongly influenced by the values of water to silicon ratio designated as r . Depending on the value of r , materials with different properties can be obtained, e.g. $r = 3.8$ or 5.1 amorphous xerogel [2], $r = 6.2$ aerogel [3], $r = 10.9$ advanced coating materials, $r = 1/2$ fibres [4] and $r = 20/50$ monodisperse nanospheres (see **Figure 2**) [5].

Reaction mixture pH strongly influences the structure and porosity of these materials [6]. Longer siloxane chains formed in $\text{pH} < 7$ are less tightly packed giving the structure of 'cross-linked spaghetti' having long and narrow pores. Highly branched siloxane chains produced in $\text{pH} > 7$ can form so-called Eden clusters with further condensation to 'raisin buns' having cylindrical pores (see **Figure 3**) [7].

Moreover, the parameters of drying process and the subsidiary substances added to the reaction mixture during sol-gel process strongly influence the pore size and their distribution. Medium porosity materials, so-called xerogels, are formed during the evaporation of solvents in normal conditions, and drying in supercritical conditions gives very porous aerogel.

The innovative, original methods of manufacturing of silica-containing nanospheres and silica aerogels were developed in the Industrial Chemistry Research Institute during recent years. Sol-gel-derived functionalized and non-functionalized silica and silica-titania nanospheres of the designed architecture tailored to the needs of the potential application were developed [8, 9].

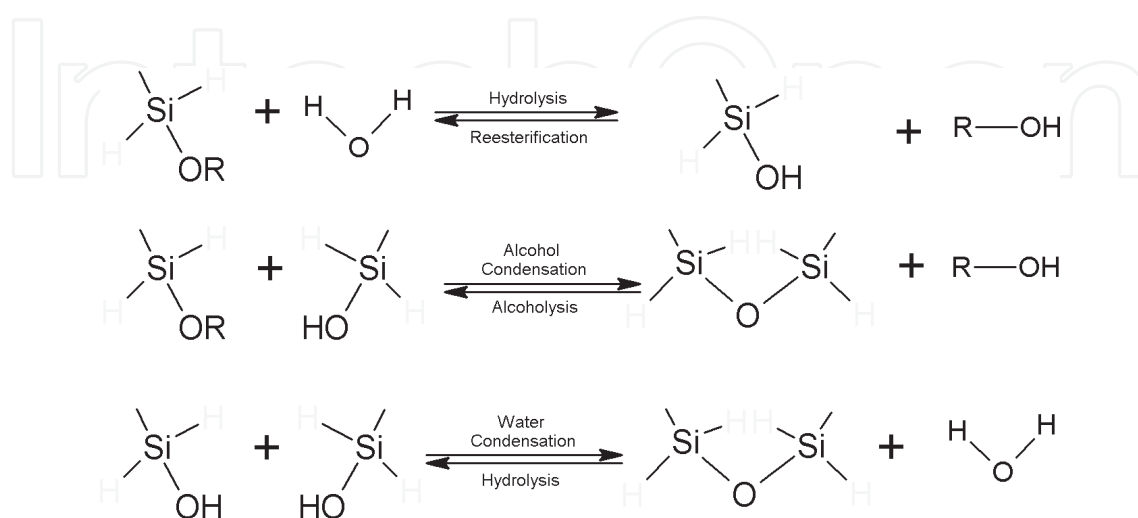


Figure 1. Simultaneous reactions of hydrolysis and condensation occurring in sol-gel process, where R is alkyl.

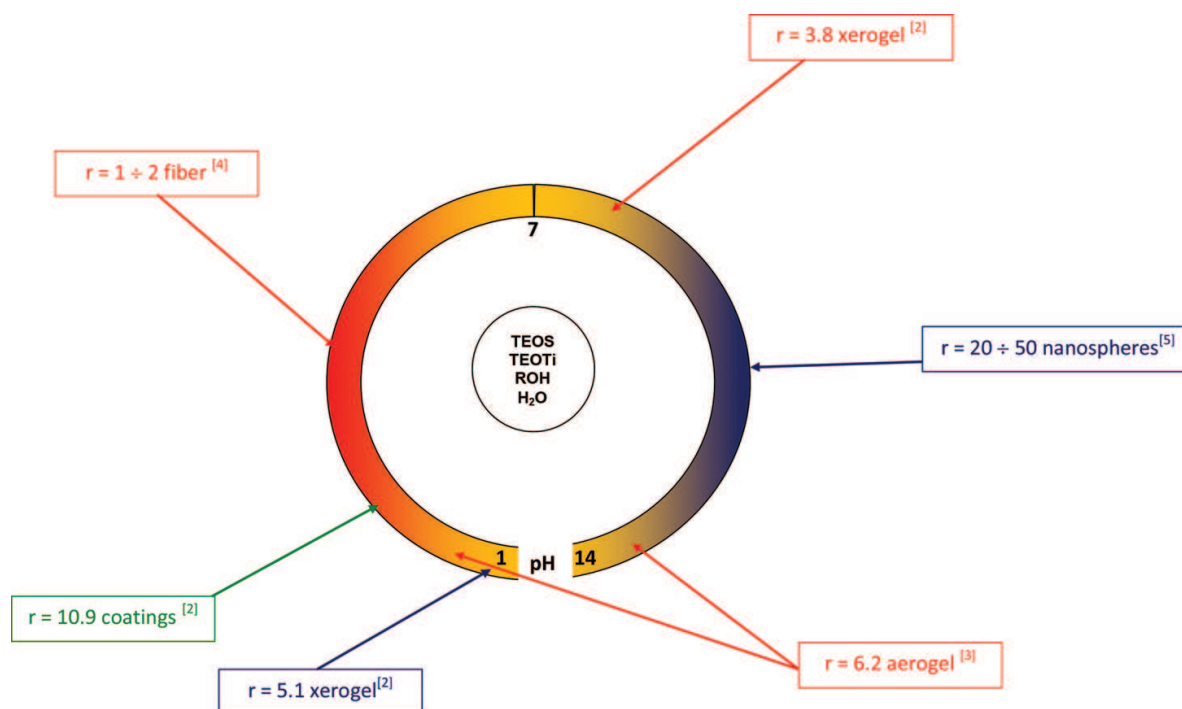


Figure 2. The effect of pH and r on physical properties of sol-gel-derived products.

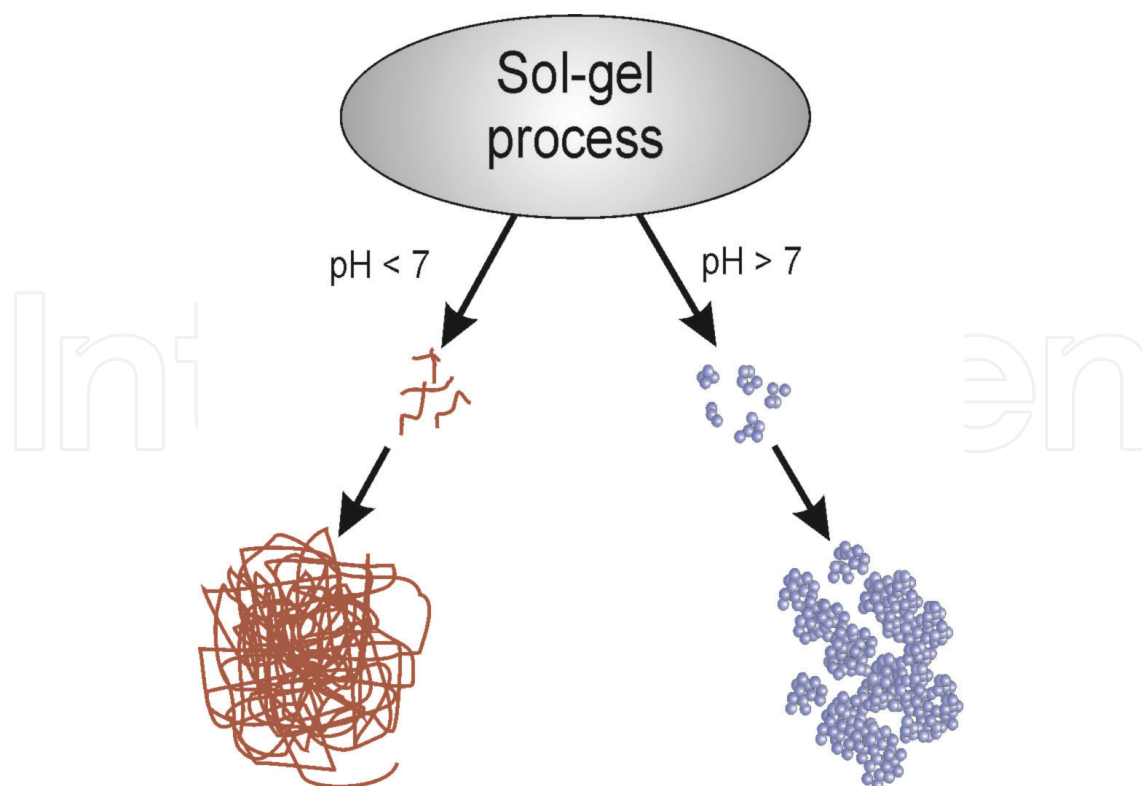


Figure 3. The effect of pH on structure and porosity of sol-gel-derived materials.

Moreover, the technologies of silica nanospheres modified by durable immobilization of silver and/or copper nanoparticles of narrow particle size distribution were also elaborated. Sol-gel process was also applied in the innovative technology of silica aerogels obtained without using supercritical drying process. The most important advantage of the developed silicon-containing hybrids lies in their high application potential, e.g. for the production of façade paints [10], polymer nanocomposites [11–13], highly efficient insulating materials and other high-tech products for construction industry.

2. Experimental part

2.1. Materials

The following chemicals were applied in the sol-gel process:

- tetraethoxysilane (TEOS, technical grade), Wacker Chemie, Germany
- aqueous ammonia (reagent grade, 25 wt%, $d = 0.91 \text{ g/cm}^3$, POCH S.A., Poland
- ethyl alcohol (absolute, reagent grade), POCH S.A., Poland
- silver nitrate, POCH S.A., Poland
- copper acetate, POCH S.A., Poland
- distilled water (prepared in the laboratory)
- hexane (reagent grade), POCH S.A., Poland
- trimethylchlorosilane (TMCS, technical grade), Wacker Chemie, Germany
- hexamethyldisilazane (HDMS, technical grade), Wacker Chemie, Germany

2.2. Methods

2.2.1. Methods of synthesis

Functionalized and non-functionalized silica nanospheres as well as silica-titania nanospheres were obtained according to the earlier procedure [8–10]. The detailed procedure of manufacturing sol-gel-derived silica nanospheres containing immobilized silver or copper nanoparticles was presented in our earlier studies in Ref. [14].

The process for preparing aerogel was carried out at a temperature of 25–60°C with a stirrer speed of 250 rpm. Tetraethoxysilane (TEOS) was used as a silica precursor. Synthesis was carried out in an aqueous-ethanolic reaction mixture using weight ratio of TEOS:H₂O:EtOH as 1:3.5:3.9. In the first phase, the pH of the reaction mixture was kept ~3. In order to start the gelation process, the pH was increased to 8 by adding liquid ammonia. The obtained

silica-based sol was poured into the prepared mould and allowed to gel. An advantage of the invention is to carry out the modification process by silanization of gel obtained in the sol-gel process. The resulting gel is subjected to age by carrying out in two stages at atmospheric pressure initially at 60–80°C for 12–24 h and then at 180–400°C. Transparent, water-repellent, ultralight aerogel granules were obtained [15].

2.2.2. *Methods of testing*

FT-IR spectra in the mid-IR range were recorded on PerkinElmer System 2000 spectrometer using KBr pellets or on KRS crystals in the purpose to observe characteristic bands of obtained materials as described earlier [10]. Particle size (Z-average diameter) and particle size distribution in resulting sols of non-functionalized, functionalized and modified silica nanospheres were measured using photon correlation spectroscopy (PCS) and Malvern apparatus (Zetasizer Nano ZS) according to the presented earlier method [14]. Scanning electron microscopy (SEM) was performed using a JEOL JSM-6490LV operating in the high vacuum mode at an accelerating voltage of 15 kV to compare the morphology of silica nanoparticles [10]. The oxidation level of silver and copper immobilized on silica nanospheres was confirmed by powder X-ray diffraction (XRD) using Siemens D500 X-ray powder diffractometer with high-resolution solid-state detector Si[Li] (operating parameters $U = 40$ kV and $I = 30$ mA) and radiation CuK ($\lambda = 0.1541837$ nm). Silver or copper content was determined by absorption atomic spectroscopy using 5100 PC, Perkin Elmer AAS Spectrometer.

Analysis of the specific surface area by the Brunauer-Emmett-Teller (BET) method was performed using a TriStar II 3020 V1.03, Micromeritics. The principle of measurement of the specific surface area is based on the measurement of the low-temperature (77 K) adsorption of inert gas (usually nitrogen or argon) at various adsorbate pressures. Based on the determined isotherms total pore volume, distribution volume, surface area and the average radius were determined by Barrett-Joyner-Halenda (BJH) method.

The bulk aerogel density was also calculated, on the basis of their mass-to-volume ratio. Hydrophobic properties of aerogels were tested by placing a small sample (approx. 1 cm²) in a vessel filled with distilled water at a temperature of 22°C. The sample that floated on the water surface for a minimum time of 30 min and immediately come to the surface after the forced immersion was classified as hydrophobic.

The thermal conductivity of aerogels was measured using FOX200 apparatus, TA I Instruments. FOX plate apparatus 200 is equipped with two sensors of heat flow density (upper and lower). It meets the requirements of ISO standards and PN-EN for this type of devices. The volume of the measured sample was determined by the properly prepared frame of the size 10 × 10 × 0.5 cm (length, width, height).

Emission of dust releasing during the procedure of the thermal conductivity of silica aerogels was measured. Measurements were done by Central Institute for Labour Protection-National Research Institute. Quantitative concentration of particles (number of particles/cm³) over time (minutes) was measured by using DiscMini apparatus, Matter Aerosol.

2.3. Results and discussion

2.3.1. Non-functionalized silica and silica-titania nanospheres

Silica and silica-titania nanospheres were obtained by sol-gel process using tetraethoxysilane and tetraethoxytitanate as alkoxysilane and alkoxytitanate precursors at a temperature of 25°C in various process conditions at pH >7, according to the reaction (see **Figure 4**).

Pure silica or silica-titania nanospheres were obtained after drying of resulting homogeneous, opaque sols. The preliminary results confirmed the completion of the hydrolysis reaction of Si—O—C bonds in alkoxysilane precursor what was justified by IR spectrum not revealing any content of organic material, in particular in the region of stretching vibrations C—H at 2900 cm⁻¹ what has been thoroughly discussed previously [10].

Homogeneous structural properties of synthesized materials were achieved due to carefully selected parameters of sol-gel process (pH, temperature, dosing rate). The technology offers a possibility to control the grain size and uniformity of nanospheres by process parameters. The smallest nanosphere size is 10 nm and the largest 600 nm. The monomodal particle size distribution and very low dispersion of particle size were observed for homogeneous sols obtained by sol-gel process (see **Figure 5**).

The preliminary results concerning the effect of temperature and stirring rate confirmed that different conditions of sol-gel process play an important role in the growth, polydispersity and stability of nanoparticles [14]. The optimization of silicon-containing hybrid synthesis using sol-gel process was carried out for silica-titania nanospheres by using the statistically designed factorial experiment which was considered to be the best method of finding the optimal formulation and process conditions. The scope of the optimal recipes of the sol-gel system was determined based on a factorial experiment designed as a 2² array with additional 'star' experimental points to obtain greater accuracy of the resulting regression equations. The software, "Statistica" 5.5—StatSoft Poland Ltd., was applied for the mathematical calculations and for the visualization of the results as contour plots. One possible approach that can be applied to the selection of the optimal formulation is presented in **Figure 6**, where the area of the optimal silica-titania properties is hatched.

Factorial design is the most suitable tool for this optimization, since it allows simultaneous determination of the effect of the parameters characterizing the properties of the sol and the obtained silica-titania nanoparticles, especially their catalytic activity in the reaction of cyclohexanone

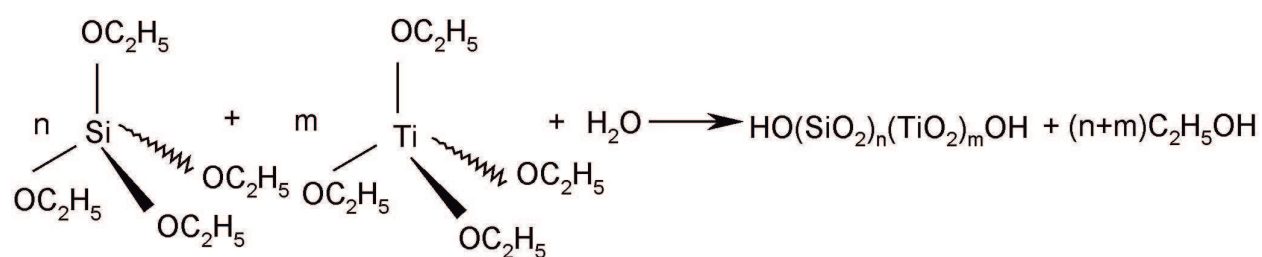


Figure 4. The reaction scheme for the preparation of silica-titania nanospheres.

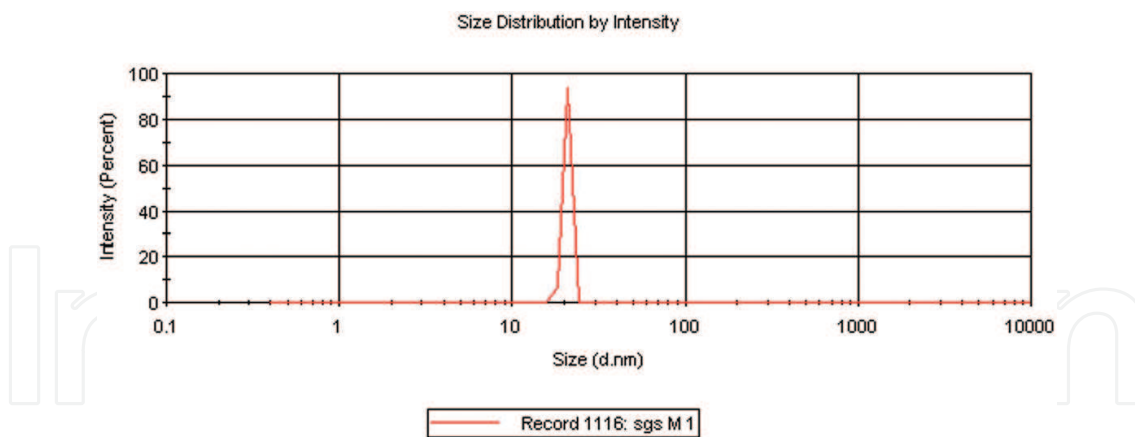


Figure 5. Monomodal particle size distribution of non-functionalized silica nanospheres of 20 nm.

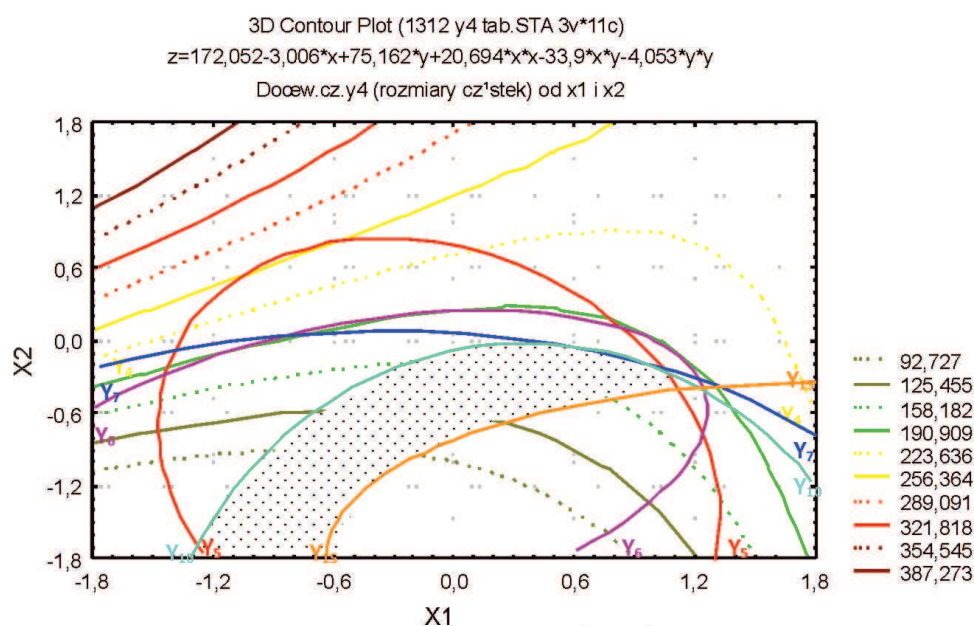


Figure 6. Determination of the area of optimal recipes (hatched).

ammoxidation. Testing of catalytic activity of obtained silica-titania nanoparticles was an integral part of the designed factorial experiment in the purpose to optimize the composition and catalytic properties of these materials. The determined parameters of the catalytic activity of nanoparticles were taken as dependent variables in the designing of factorial experiment. The area of optimal sol recipes and properties of silica-titania nanospheres was obtained by overlapping, on the contour plot of the selected dependent variable, the contour lines obtained for the assumed limiting values of the other critical dependent variables. The following dependent variables y_i were considered: y_4 - particle size [nm]; y_5 - particle size distribution [nm]; y_6 - polydispersity; y_7 - sol appearance; y_{10} - cyclohexanone oxime yield (mol%); and y_{15} - consumption of H_2O_2 on cyclohexanone oxidation. The limiting values of variables x_1 and x_2 in the area of optimal properties are presented in **Table 1**.

Real values of the independent variable	From	To
X_1 -Ti/Si ratio (mol%)	1.217	8.201
X_2 content of NH_{3aq} in sol (wt%)	0.660	0.875

Table 1. The limiting values of variables x_1 and x_2 in the area of optimal properties.

In order to synthesize silica-titania nanoparticles with optimal properties, the values of x_1 and x_2 variables corresponding to the selected value of the variable y_i should be selected within the hatched area. Silica-titania nanospheres prepared according to the recipes from the area of optimal properties were characterized by homogeneous particle sizes, as illustrated by SEM micrograph (see **Figure 7**).

Supramolecular structure of received Si-containing nanospheres depends considerably on the method of drying. Drying in the oven drier allows to obtain separate nanoparticles, while after drying in spray drier, spherical microstructures can be observed (see **Figure 8a, b**).

The differences in the structure of the microaggregates composed of silica or silica-titania nanospheres can be easily observed. Silica nanosphere microaggregates are composed of single nanoparticles, whereas silica-titania aggregates have solid structure. The observed differences may have a significant impact on the redispersibility of the received nanomaterials used both as nanofillers and catalysts.

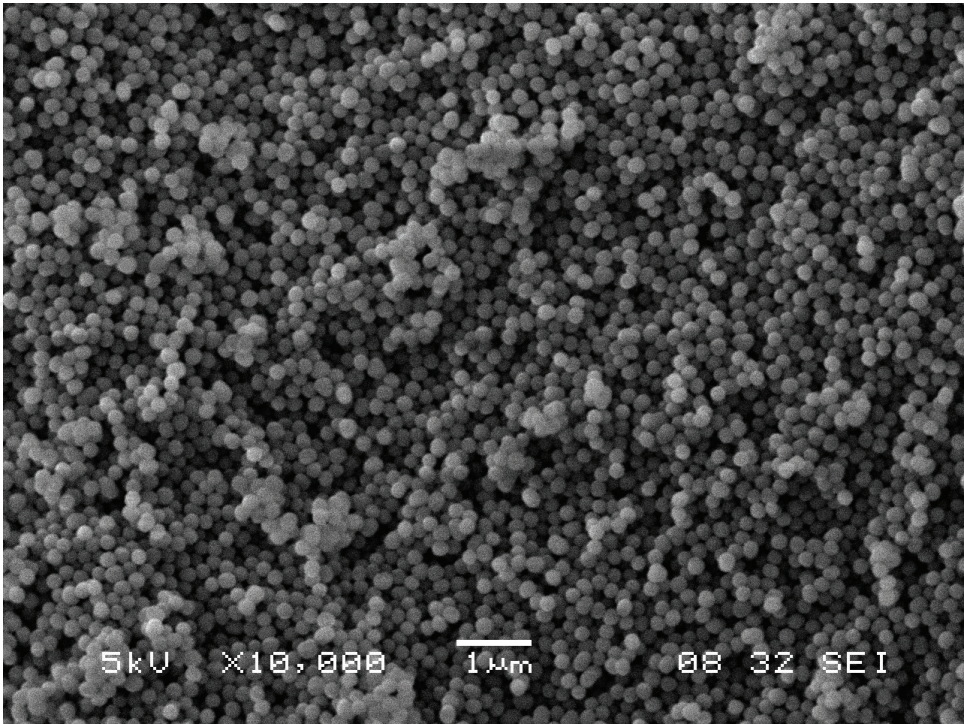


Figure 7. SEM micrograph illustrating homogeneous particle size distribution of silica-titania nanospheres (sample dried in oven drier).

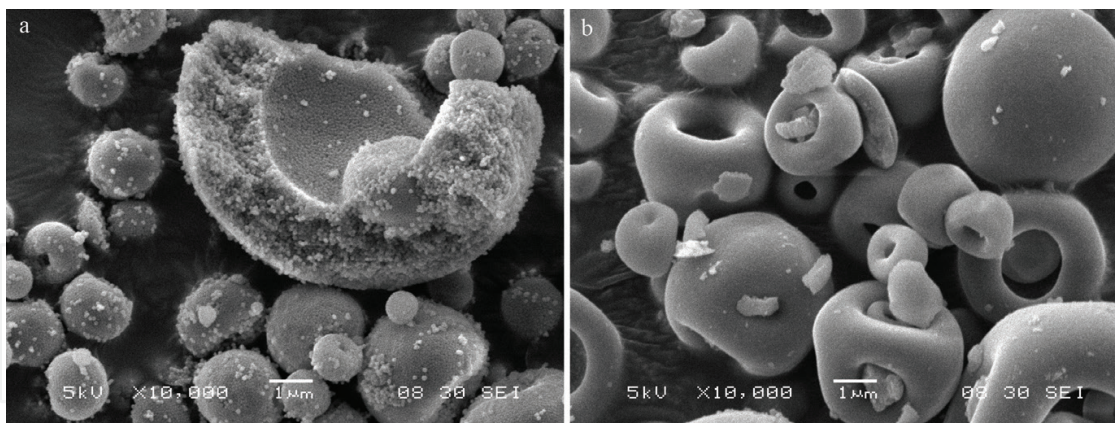


Figure 8. SEM micrographs of nanospheres dried in spray drier (a) silica nanospheres and (b) SEM silica-titania nanospheres.

Very promising results confirming the use of these nanomaterials as nanofillers were received. Thus, the sol of non-functionalized silica nanospheres having a particle size of about 50 nm was applied as poly(vinyl chloride) (PVC) nanofiller, which was introduced during the suspension polymerization process. The resulting PVC composite showing the homogeneous distribution of silica nanospheres was characterized by significantly improved mechanical properties, already at a content of 0.5 wt% of these nanoparticles [16–18].

2.3.2. Functionalized silica nanospheres

Functionalized silica nanospheres were developed in the purpose of permanent embedding to cross-linked polymer matrix, which should allow obtaining nanocomposites with significantly improved properties. The following reactive groups, vinyl, amino, methacryloxy and glycidyloxy, were selected and introduced through the use of suitable carbofunctional silanes according to the following reaction (see **Figure 9**).

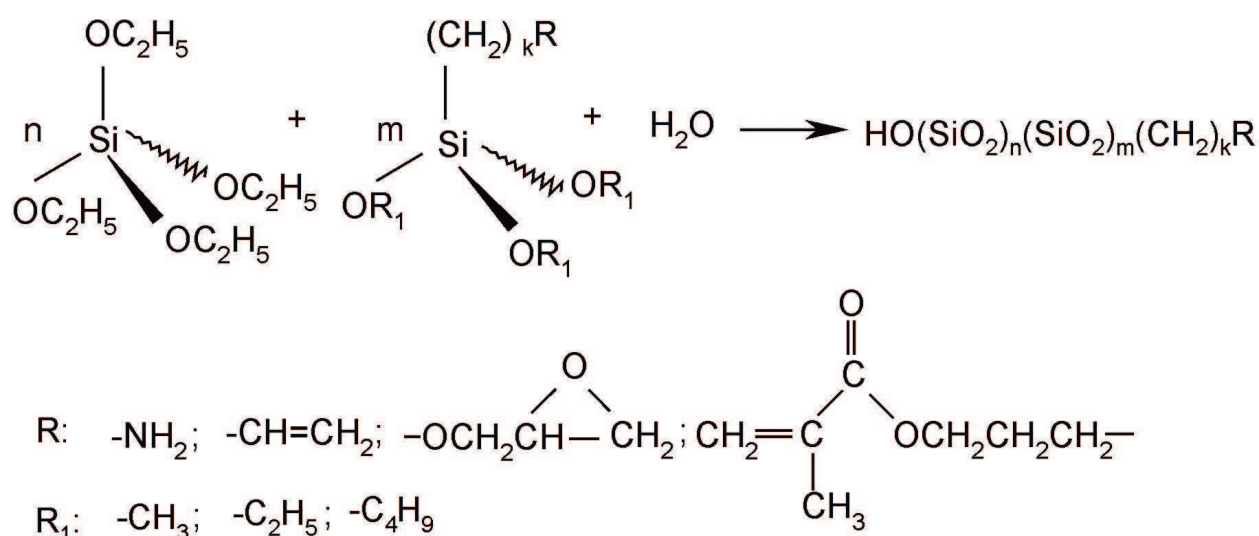


Figure 9. The reaction scheme for the preparation of functionalized silica nanospheres.

The presence of the reactive groups in functionalized silica nanospheres was confirmed based on the intensity of the following characteristic bands in the IR spectrum for vinyl group, $1640\text{--}3070\text{ cm}^{-1}$; for amine group, $1710\text{--}3300\text{ cm}^{-1}$; for methacryloxy group, $1640\text{--}1650\text{ cm}^{-1}$ and for glycidyloxy group, $1000\text{--}1100\text{ cm}^{-1}$. The applicability of silica nanospheres functionalized with vinyl groups was tested in polymer composites based on silicone rubber cross-linked by hydrosilylation reaction according to the following reaction (see **Figure 10**).

The substantial effect of the content and the average particle size of embedded silica nanospheres on the tensile strength of silicone rubber nanocomposites can be observed (see **Figure 11**).

The best results were achieved for nanoparticles characterized by a particle size of 82.4 nm added in the content range from 1.0 to 1.5 wt%. A visible decrease of tensile strength can be observed for both larger and smaller content of nanoparticles introduced in the amount of 2 and 0.5 wt%, respectively. Silica nanospheres functionalized with amine, glycidoxyl and methacryloxyl groups were successfully applied for manufacturing of polymer nanocomposites based on polyamide, polyolefins and other engineering polymers [11, 13].

2.3.3. Modified silica nanospheres by immobilization of silver or copper nanoparticles

Modification of sol-gel-derived silica nanospheres by durable immobilization of silver or copper nanoparticles was studied as the effective stabilization method of metal nanoparticles

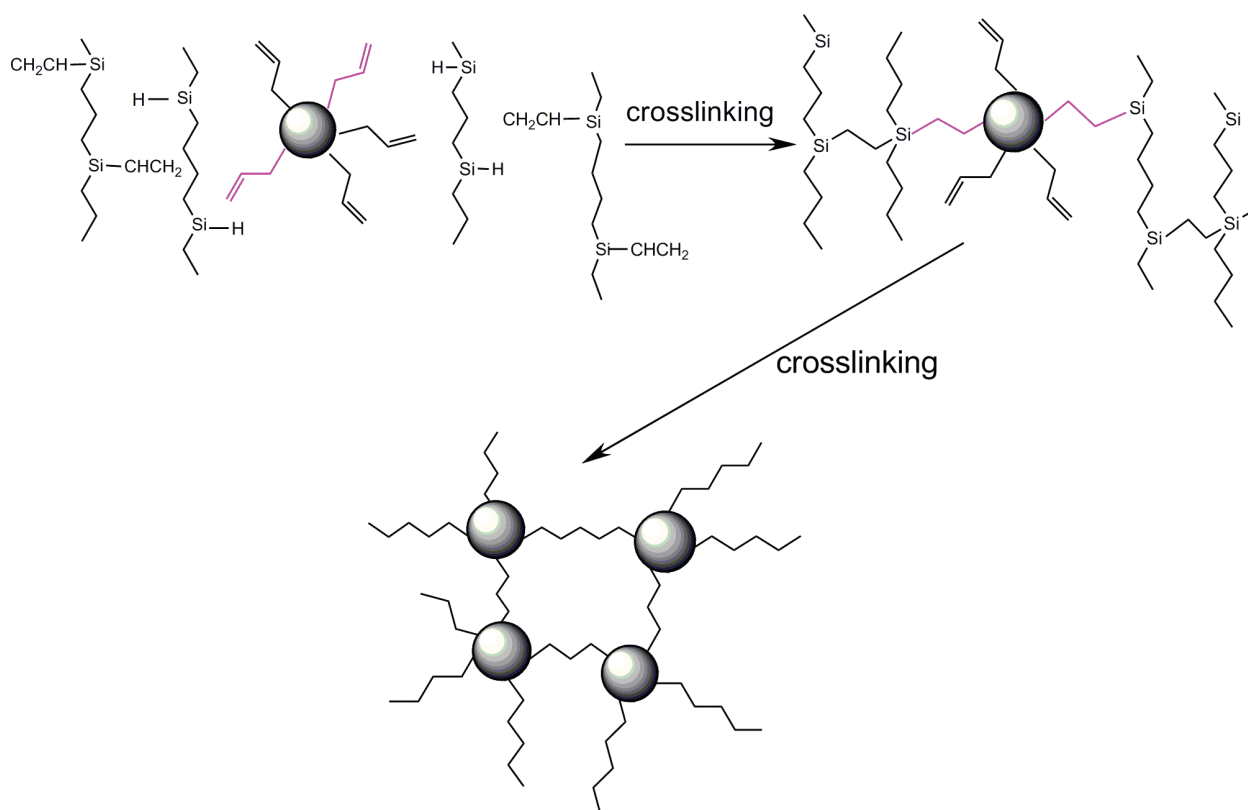


Figure 10. Scheme of formation of silicone rubber matrix with durably built-in silica nanospheres.

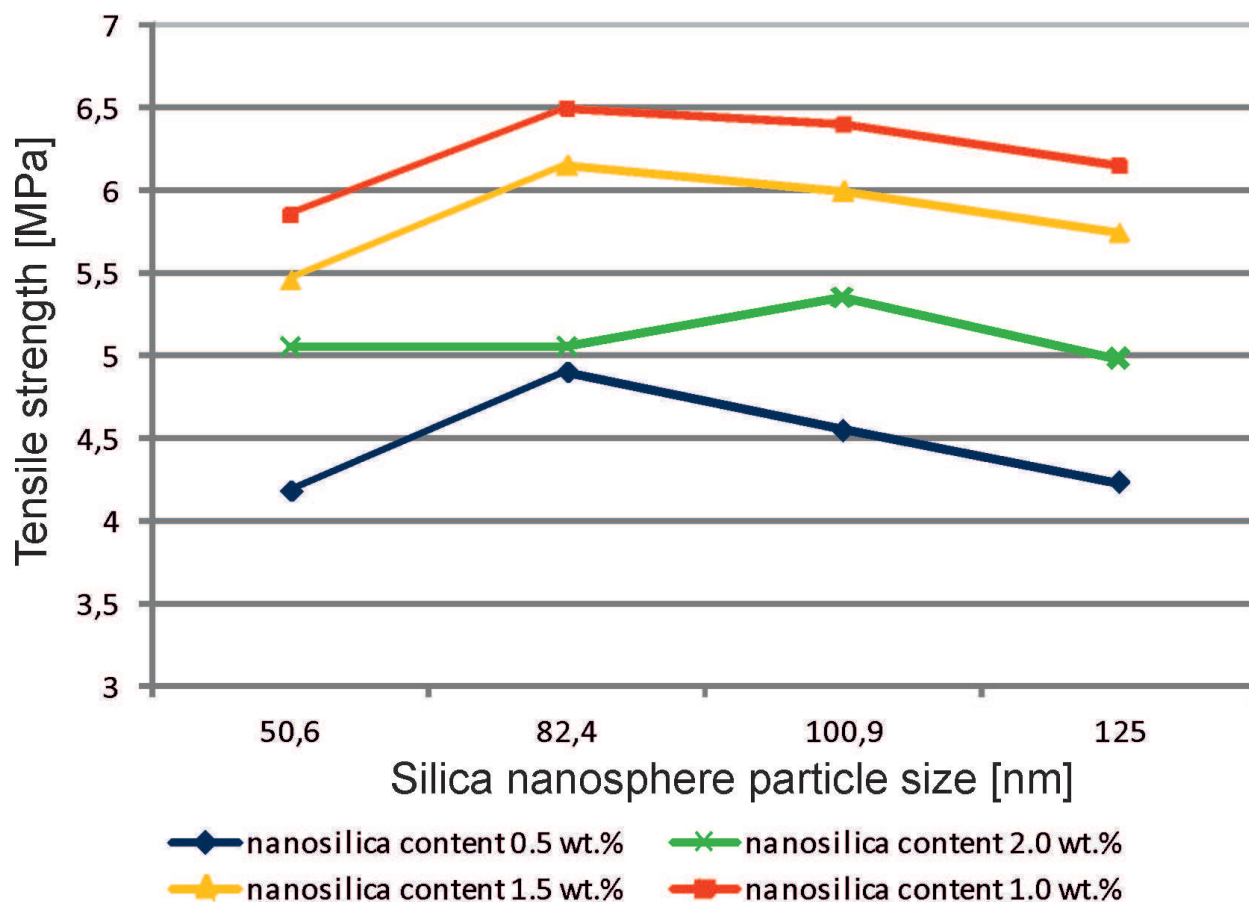


Figure 11. The effect of the content and the average particle size of embedded silica nanospheres on the tensile strength of silicone rubber nanocomposites.

against their agglomeration. However, the antimicrobial activity of silver and copper, especially as nanoparticles, has long been recognized [19, 20]; the successful application of these metals as biocides was limited due to the low stability of colloids of these nanometals. The agglomeration of silver or copper nanoparticles in colloids can result in the decrease of their biocidal effect. Nanometal particles can be stabilized by the protective colloids [21]. The application of such stabilized colloids is limited due to the negative impact of protective stabilizers on the properties of the obtained materials. Studies on the microbial activity of silver and copper have shown that both the nanoparticles of metals and their ions or colloidal solutions demonstrate biocidal activity [22]. Nanoparticles of these metals are sufficiently small to damage the bacterial cell membrane and significantly affect the function and operation of the enzymes contained in the cell [23–25].

One of the most interesting examples of protection of metal nanoparticles before agglomeration is their immobilization in the films of silica [26]. The synthesis is conducted using a sputter deposition silica film containing metal particles.

One method of Cu nanoparticle absorption into silica nanoparticles is the synthesis by ion implantation using a laser of appropriate wavelength (ultraviolet) [27, 28]. The obtained modified nanosilica can be used as active nanofiller for polymer nanocomposites.

The use of the sol-gel method is an easier way to obtain nanosilica modified by metal nanoparticles characterized by homogeneous distribution of metal nanoparticles on the silica surface [29, 30]. The exemplary SEM micrograph reveals a uniform distribution of copper nanoparticles on the surface of silica nanospheres (see **Figure 12**).

The oxidation degree of copper or silver was examined by XRD showing the diffraction peaks 110, 200, 220 and 311 that confirm the presence of Ag^0 or Cu^0 [14]. Metallic silver or copper form the cubic F type cells, the angular positions of the reflections are characteristic for silver: 38.15; 44.32; 64.49; 77.55; 6.90 or copper: 43.33; 50.48; 74.20; 90.30. Copper or silver nanoparticles incorporated in the silica structure are stable and do not undergo coagulation during storage, which ensures durable biocidal activity and solves the problem of the loss of properties due to the agglomeration of silver or copper nanoparticles.

Several results of antimicrobial activity of the obtained silica nanospheres containing immobilized silver or copper nanoparticles [10] as well as of polymer nanocomposites containing these fillers [12] were reported earlier. Recently, interesting application results of anti-algae and antifungal activity of silica nanospheres containing immobilized copper nanoparticles used as silicone-acrylic paint nanofillers were obtained (see **Figure 13a–c**).

It can be easily observed that the growth of algae on the surface covered by silicone-acrylic paint containing 0.5 ppm of copper nanoparticles immobilized on silica nanospheres having a particle size of 80 nm was completely stopped (**Figure 13a**), while the untreated control sample was almost completely overgrown with algae (**Figure 13b, c**).

Summarizing the results of the performed research on silica nanospheres, it should be underlined that this is a very promising area of research that allows the use of the developed silica-based nanomaterials for innovative and original applications.

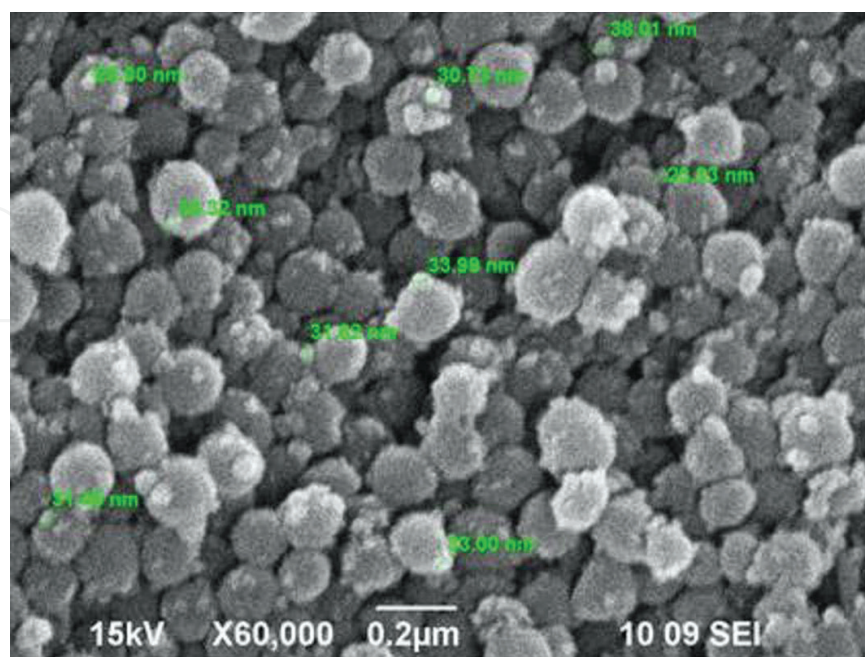


Figure 12. SEM micrograph of silica nanospheres containing immobilized silver nanoparticles.

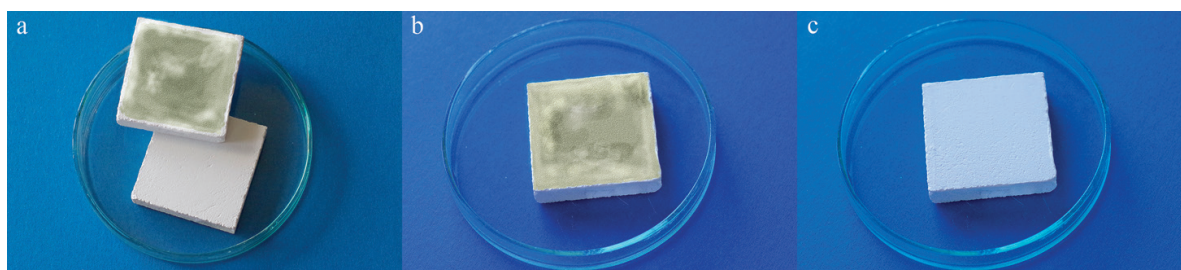


Figure 13. Anti-algae activity of copper nanoparticles immobilized on silica nanospheres applied as filler of silicone-acrylic paint: (a) sample protected with silicone-acrylic paint showing no algae growth and control sample overgrown with algae, (b) control sample after 4 weeks of weathering before testing anti-algae activity and (c) tested sample after 4 weeks of weathering before testing anti-algae activity.

2.3.4. Sol-gel-derived silica aerogels

Aerogels belong to the class of the advanced materials. Specific properties of the aerogels are resulting from their unique composition in which 90–98% is air and the rest is silica forming the three-dimensional structure. The air entrapped in the aerogel is the key agent that gives unique characteristics giving the enormous potential for various applications. The unique properties include low density, very high specific surface area, porosity and low thermal conductivity. Aerogels are non-toxic, environmentally friendly and fire resistant (melting point 1200°C) what make them ideal insulating material both thermal and acoustic [31]. Insulation - mainly thermal) is an important portion of the building materials market [32, 33]. Therefore, aerogels were in the spotlight of researchers and become a medium of inspiring all who see their unique properties used in the practical application.

However, the main problem associated with the extensive use of silica aerogels is their high price and complex production process. Moreover, a serious disadvantage of silica aerogels is their dustiness. The development of cheaper methods of production undoubtedly will increase their area of application [34]. Formation of a wet gel, which is a product of hydrolysis and polymerization (condensation) and drying as the second important process, which is a critical step in the creation of the spatial structure of aerogels, see **Figure 14**.

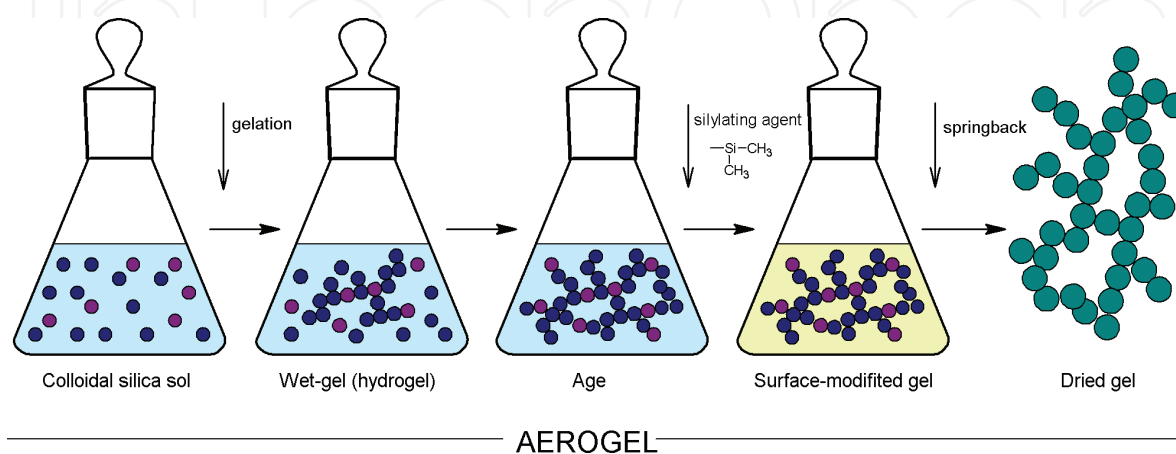


Figure 14. Aerogel manufacturing scheme.

During typical procedure gel should be aged and modified (if needed) and then dried with total removal of all liquids from the pores.

Gel ageing is needed to strengthen its structural and mechanical properties. This results in the increase of the three-dimensional network cohesion by creating new bridge bonds $\equiv\text{Si}-\text{O}-\text{Si}\equiv$ which results in the shrinkage of the gel matrix. This is connected with water and alcohol release from the pores (syneresis). This process has a major effect on the porosity of the final product; therefore, it is important to control the conditions under which the ageing takes place, i.e. temperature and time. The next step is immersion of gel in a suitable anhydrous organic solvent, e.g. hexane, which inhibits the formation of hydrogen bonds and also leads to a reduction of capillary forces helping in porosity increase. Thus, prepared gel is subjected to a modification by using silylating agent in the purpose of hydrophobic group introduction [35]. The modification process is necessary to replace the reactive OH groups with non-reactive CH_3 groups to avoid the formation of siloxane bridges at the pore walls (see **Figure 15**).

The drying step is the greatest technological challenge. During the drying process, the residual solvents are removed that causes weight loss of the product with a simultaneous increase in volume. Incorrect parameters of the drying can result in the reduction of gel porosity.

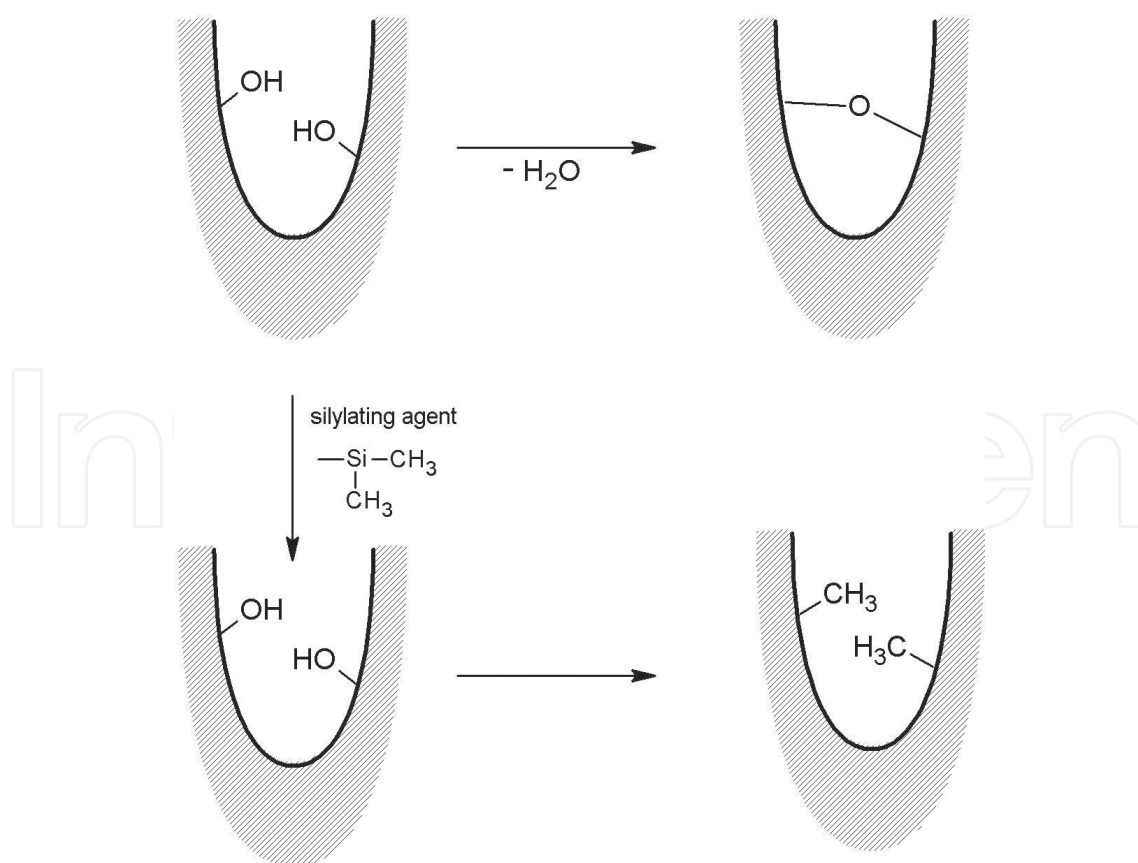


Figure 15. The replacement of the reactive OH groups with non-reactive CH_3 groups.

Several methods of aerogel drying are used. The main known from the literature is the drying under supercritical conditions [36, 37], but this method is expensive and complicated and requires specialized equipment.

In our studies, we were focused on the development of original aerogel technology. The key point of this technology is the process of drying at atmospheric pressure, which has simple experimental equipment requirements and easy to control test parameters [15].

Several samples of silica aerogel using tetraethoxysilane as a precursor at a fixed ratio of the main reactants in the sol-gel process were prepared (see Section 2.2.1). For all described silica aerogel samples, the same procedure of sol manufacturing was applied. Differences in the properties of aerogel samples result from the application of different gel treatment procedures. Technological parameters of gel treatment procedure are presented in **Table 2**.

Samples A4 and A5 obtained in a pilot scale, the remaining samples were obtained at a laboratory scale.

The obtained silica aerogels are transparent, water repellent and very light. Dustiness to a large extent had been reduced, which is important from the point of view of their application. Satisfactory results of the thermal conductivity in the range of 0.024–0.038 W/(mK) were obtained. As a control sample commercial silica aerogel SJ1800Series (CHKAM) was used. The results obtained for the selected samples are shown in **Table 3**.

The lowest thermal conductivity was measured for the sample A-1. In order to confirm the obtained result, two other samples (A-8 and A-9) were prepared according to the same

Sample	Ageing time (h)	Silylating agent	Drying method and temperature (°C)
A-1, A-8, A-9	48	TMCS	180
A-2	48	TMCS	Muffle furnace 400
A-3	336	TMCS	180
A-4	48	TMCS	180
A-5	48	HDMS	180
A-6	48	TMCS	Oven 60
A-7	48	TMCS	Oven 60
A-10	48	TMCS	Oven 200
A-11	48	TMCS	Oven 200
A-10	48	TMCS	Oven 250
A-12	48	TMCS	Oven 300
A-13	48	TMCS	Muffle furnace 400
TMCS, trimethylchlorosilane; HDMS, hexamethyldisilazane			

Table 2. Technological parameters of gel treatment procedure applied for samples A-1–A-13.

Sample	Specific surface S_{BET} (m^2/g)	Total pore surface (m^2/g)	Pore size (nm)	Total pore volume (cm^3/g)	Thermal conductivity ($\text{W}/(\text{mK})$)	Bulk density (g/cm^3)
Control sample CHKAM	507	123.78	22	2.87	0.030	0.030
A-1	565	185.16	21	3.07	0.025	0.074
A-2	978	989.44	13	3.31	0.029	0.031
A-3	868	194.06	9	2.05	0.038	0.056
A-4	689	292.56	15	2.62	0.030	0.0843
A-5	667	498.92	10	1.07	0.033	0.1735

Table 3. Characteristics of the selected sample.

procedure. The values of thermal conductivity obtained for samples A-8 and A-9 confirm the repeatability of the synthesis procedure.

The key indicator of silica aerogel properties is also their porous structure. For this purpose, a measurement of the specific surface area by the BET method was applied for selected samples. Nitrogen adsorption isotherms reflect the structure of the porosity of studied adsorbents in Ref. [14].

The observed BET specific surface area for the silica aerogel was in the range from 565 to 978 m^2/g , and the total pore volume was in the range of 1.07–3.31 cm^3/g . The measured bulk density values indicate the lightness of the obtained sample that is in good accordance with the published data [34, 38].

Isotherms obtained by low-temperature nitrogen adsorption indicated that the obtained materials are mesoporous (see Figure 16).

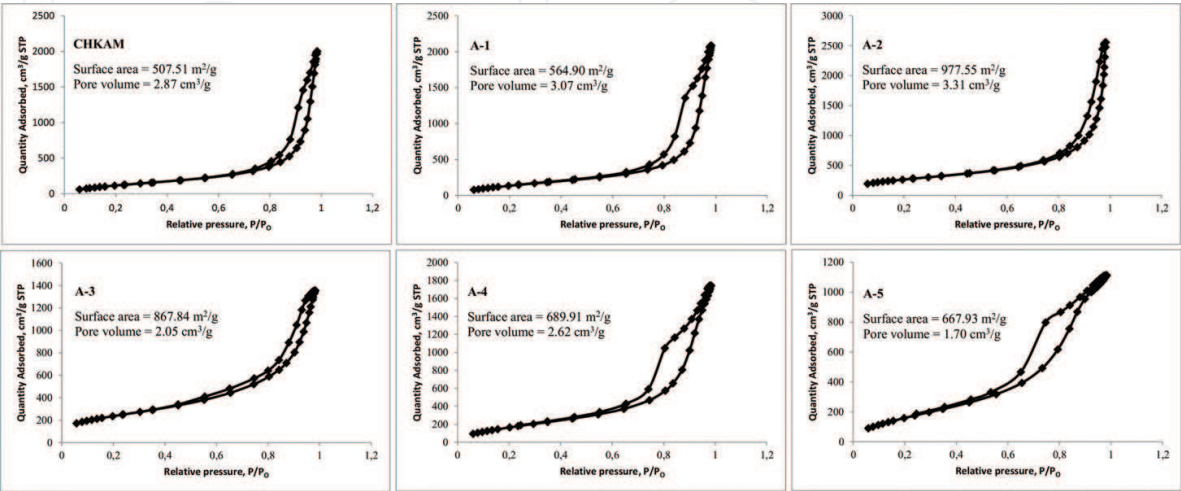


Figure 16. N₂ adsorption-desorption isotherms at 77 K for the silica aerogel.

According to the IUPAC classification [39, 40], the shape of the isotherms can be described as type IV with H2 hysteresis loop (samples A-1, A-4, A-5) or H3 (samples CHKAM, A-2, A-3), which indicates the presence of pores in the shape of 'ink bottle' or cylindrical.

More complete information about the texture of the tested adsorbent materials can be obtained based on an analysis of the distribution curve of the pore volume (see **Figure 17**).

On this basis, the structure of the adsorbent can be concluded. All curves are shown in one scale; the pore diameter distribution is in the range from 2 to 100 nm, confirming the high proportion of mesopores in the structure of adsorbents (according to the IUPAC classification) [39, 40].

The narrow size of the peaks in the samples A-4 and A-5 indicates the high homogeneity of pore size. A wider range of sizes of the peaks in the sample A-2 are due to the presence of pores of different diameters. This affects a very large surface area of the adsorbent (**Table 1**). The pore size distribution in the samples CHKAM, A-2 and A-3 is heterogeneous, where we find more than one peak and a broad range of pore sizes.

The effect of drying temperature under atmospheric pressure conditions on the thermal conductivity coefficient of obtained aerogels, was studied (see **Table 4**).

The samples were dried in a convection plate oven or in a muffle furnace. The best results of thermal conductivity were obtained for the samples dried in the convection plate oven at 180°C.

Drying under atmospheric conditions, it is a promising technique [41], which could be used on an industrial scale, as demonstrated in the verification process carried out on a prototype, large scale laboratory line for the production of aerogels.

As mentioned earlier, one of the major disadvantages of the silica aerogels is their dustiness which is the tendency of a material to release the dust into the atmosphere during manufacturing and use of the material, defined as the amount of dust emitted during the standard test procedure

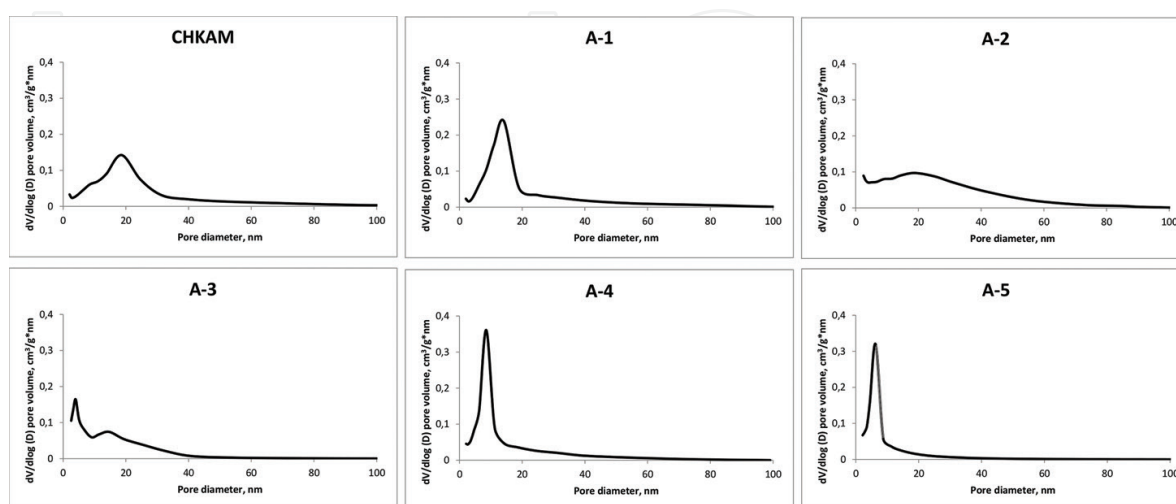


Figure 17. BJH pore size distribution of silica aerogel.

Sample	Thermal conductivity (W/(mK))	Drying method and temperature (°C)
A-6	0.035	Oven 60
A-7	0.030	Oven 60
A-8	0.025	Oven 180
A-9	0.024	Oven 180
A-10	0.033	Oven 200
A-11	0.031	Oven 200
A-10	0.034	Oven 250
A-12	0.031	Oven 300
A-13	0.028	Muffle furnace 400
A-2	0.029	Muffle furnace 400

Table 4. Thermal conductivity of silica aerogel terms of drying method.

application. This parameter depends not only on the properties of the material but also on the testing method [42]. In the present case, dust emission measurements during the test procedure related to measurement of thermal conductivity of the obtained silica aerogel and comparative sample were realized. These studies confirmed the significantly lower emissions of the obtained silica aerogel when compared to the control sample (see Figure 18).

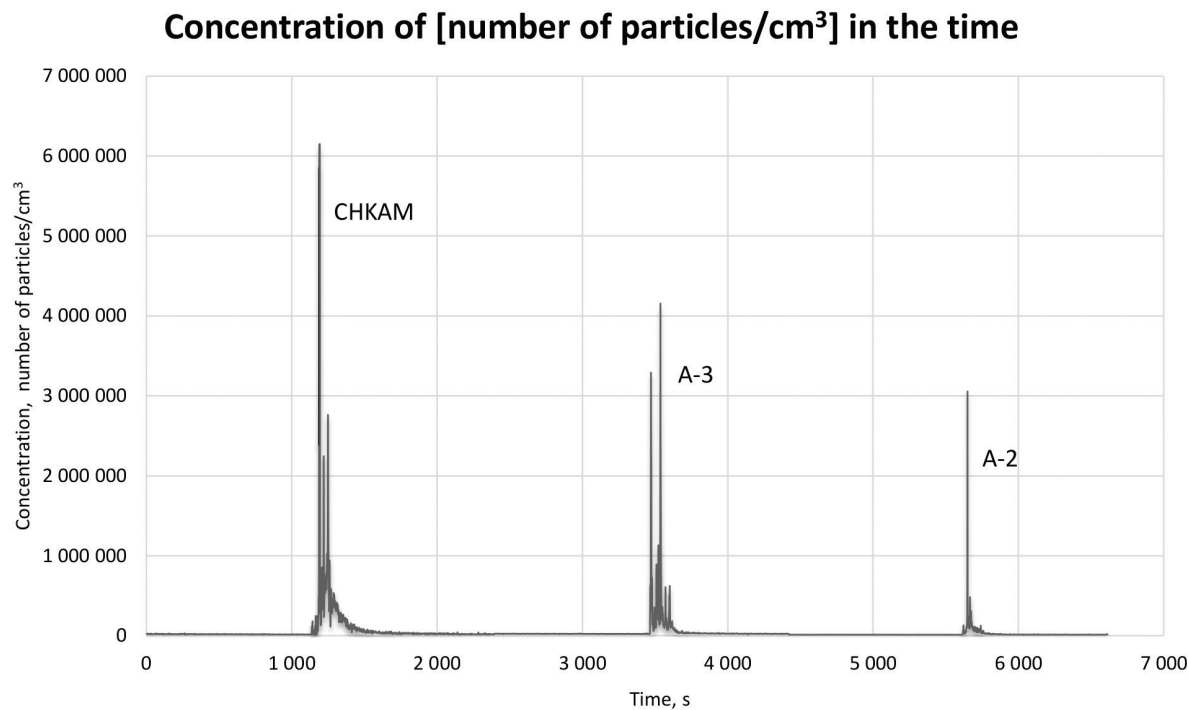


Figure 18. Emissions of dust from aerogels defined as the concentration of particles in 1 cm³.

The main advantage of aerogel drying at atmospheric pressure is connected with the fact that it does not require high pressure and can be carried out continuously. This has a significant impact on the economy and ecology of the process of aerogel manufacturing. Such aerogel is a perfect component of construction products improving their thermal insulation properties. Moreover, such aerogel can be used in all applications where its lightness, non-toxicity and low coefficient of thermal conductivity as well as its hydrophobicity are needed.

2.3.5. Concluding remarks

The optimization of the synthesis of sol-gel-derived silicon-containing hybrids was carried out under different conditions of temperature and stirring rate confirming that the stirring rate plays an important role in the growth, polydispersity and stability of nanoparticles. Supramolecular structure examination proved homogeneous structure of the obtained silica nanopowders and aerogels. The most important advantage of the developed silicon-containing hybrids lies in their high application potential, e.g. for the production of façade paints, polymer nanocomposites, highly efficient insulating materials and other high-tech products for construction industry. The application of the developed additives allows to achieve higher hygienic level with the significant decrease of the applied amount of aggressive biocides, which are harmful to human health.

Acknowledgements

This work has been financially supported by projects No UDA-POIG.01.03.01-00-073/08-00 and No UDA-POIG.01.03.02-14-074/10-00 co-financed by the EU (European Regional Development Fund) and project GEKON1/O2/213318/14/2014 co-financed by the National Centre for Research and Development and National Fund for Environmental Protection and Water Management in Poland.

The authors thank Dr. Eng. Elzbieta Jankowska from the Central Institute for Labour Protection - National Research Institute for the measurements of dust emission, Dr. Eng. Osazuwa Osawaru from the Industrial Chemistry Research Institute for the measurements of surface area and Dr. Aneta Łukomska of the Industrial Chemistry Research Institute for preparation of SEM micrographs and Mr. Marek Panasiuk of the Industrial Chemistry Research Institute for measurements of particle size, thermal conductivity and all technical assistance.

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