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Synthesis and physicochemical characterization of silica fillers modified with octakis({3-methacryloxypropyl}dimethylsiloxy) octasilsesquioxane

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Hybrid nanofillers of silica grafted with octakis({3-methacryloxypropyl}dimethylsiloxy) octasilsesquioxane were obtained by the method based on solvent evaporation with the use of both hydrated or emulsion spherical silica. Octakis({3-methacryloxypropyl}dimethylsiloxy) octasilsesquioxane was applied as a modifying agent and it was synthesized by employing the hydrosilylation reaction. The effectiveness of modification of the hybrid nanofillers obtained was verified using Fourier transform infrared spectroscopy and nuclear magnetic resonance (^{29}Si and ^{13}C CP MAS NMR). The products obtained were characterized by determination of their physicochemical properties and porous structure, including specific surface area, pore diameter and pore volume. Dispersion degree and particle size of the nanofillers was characterized by NIBS (Non-Invasive Back-scatter) method and laser diffraction technique, while their morphology by transmission electron microscopy.

Keywords: octasilsesquioxane; silica; functionalization; hybrid nanofillers.

INTRODUCTION

Silsesquioxanes form many structures but the cage ones, known also as polyhedral oligomeric silsesquioxanes (POSS), have found the widest application. They make nanometric systems of the general formula $(RSiO_{1,5})_n$, where R is hydrogen, chlorine or an organic group. Thanks to a diversity of substituents, POSS make unique structures which usually appear as a result of hydrolysis and condensation reactions of trialkoxy- or trichlorosilanes[1–4]. As a single cubic structure (T_8) can accept as many as 8 groups, the compounds solubility, catalytic activity or adhesive properties can improve[5]. Cage silsesquioxanes make a new group of compounds alternative to siloxanes. POSS are nontoxic and relatively reactive, they also show significant chemical resistance[6]. So far they have been subjected to a large number of tests. Among others they have been used in polymer/POSS systems in order to achieve e.g. an increase in the cross-linking temperature or change in some other properties[7–16].

Although they show many attractive properties, they are not widely used mainly because of the cost and problems with their synthesis to get well-defined structural, dispersive and chemical properties[17]. Because of their interesting features, an attempt was made to combine them with silica, which is a relatively cheap material. Silica is highly susceptible to chemical modifications thanks to the presence of silanol groups on the surface or in the internal structure. These groups also determine the hydrophilic character of silica. Moreover, on the silica surface there are non-reactive siloxane groups responsible for silica hydrophobic character[18]. The wide use of silica stems from its physicochemical properties. It is used as polymer filler, in glass industry, construction industry, nanotechnology (production of silica nanostructures and hybrid materials) and in electrochemical industry[19, 20], as well as in biomaterials science and biomedicine[21, 22].

The aim of this study was to develop a synthesis of new generation hybrid fillers made of SiO_2 and octakis({3-methacryloxypropyl}dimethylsiloxy) octasilsesquioxane (M-POSS). The synthesis of octasubstituted oligosilsesquioxanes was described earlier[23]. It is expected that these new hybrid materials besides application as polymer fillers, could also be applied as adsorbents or heterogenic catalysts. As yet materials of this type have not been fully characterized[24–26].

EXPERIMENTAL SECTION

Synthesis of octakis({3-methacryloxypropyl}dimethylsiloxy) octasilsesquioxane

Octakis (3-methacryloxypropyl}dimethylsiloxy) octasilsesquioxane (M-POSS) was obtained in the process based on a reaction involving hydrosilylation of allyl methacrylate ether (purchased from POCH SA) with octakis(hydroxydimethylsiloxy) octasilsesquioxane (synthesized in a two stage process in analogy to paper[27]). The reaction was carried out in an open system in the environment of toluene solvent, with the use of Karstedt's catalyst (purchased from Aldrich) in a quantity of 1×10^{-5} molPt/mol Si-H. POSS solution and allyl methacrylate ether were placed in a flask at the molar ratio 1:1.2, into which the catalyst was added. After an introduction of the catalyst, the temperature of the reaction mixture began to grow and with the help of an ice-water bath it was maintained at 45 °C. After temperature stabilization it was left at room temperature for 24 h. Then toluene and excess amount of allyl metacrylate were evaporated under high vacuum and with no additional heating of the mixture. The scheme of octakis({3-methacryloxypropyl} dimethylsiloxy) octasilsesquioxane synthesis is presented in Figure 1.

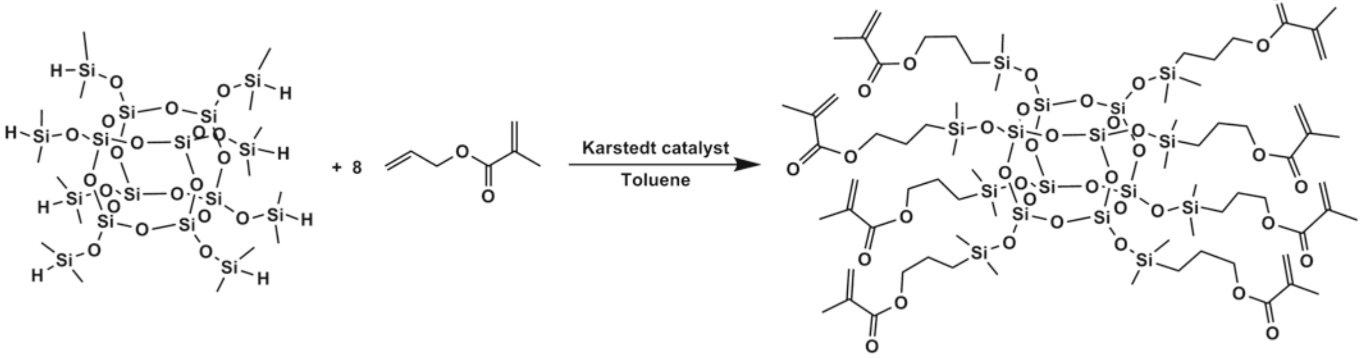

Figure 1. Synthesis of octakis({3-methacryloxypropyl}dimethylsiloxy) octasilsesquioxane (M-POSS)

Preparation of SiO_2/POSS hybrid nanofillers

The process has begun with the production of silicas on a large laboratory scale. Two types of silica were prepared. Hydrated silica (HS) was obtained in the process of precipitation from aqueous solutions of sodium silicate and sulfuric acid, as it was described earlier[28, 29]. Another silica filler was prepared in the emulsion environment (ES). The basic steps of silica production are in analogy to the previously described procedure[30].

The SiO_2/POSS hybrids were obtained by solvent evaporation method. At first a fraction of HS or ES silica was introduced into the reactor and then on the silica surface a mixture made of a M-POSS and toluene was introduced in doses by the atomization method. The modifying substance was introduced in the amounts of 3, 5 or 10 weight parts by mass (in relation to SiO_2). In further step of nanofillers formation evaporation of solvent with simultaneous modification was performed. Afterwards the samples were dried in a convection dryer (SEL–I3, Memmert) at 120 °C for 48 h. The scheme of the synthesis of SiO_2/POSS hybrids as described in detail in[31], and the scheme of chemical and physical interactions between silica and oligosilsesquioxane (M-POSS) are presented in Figure 2.

Evaluation of physicochemical properties

The final products were characterized by a number of methods. Fourier transform infrared spectroscopy (FTIR) measurements were conducted on an IFS 66v/S spectrophotometer (Bruker) at room temperature. The samples were prepared by mixing with KBr, and then pressing into small tablets. The FTIR spectra were obtained in the transmission mode between 4000 and 400 cm^{-1}.

^{29}Si and ^{13}C CP MAS NMR measurements were carried out on a DSX spectrometer (Bruker). For the determination of NMR spectra a sample of about 100 mg was placed in a ZrO_2 rotator with diameter of 4 mm, which enabled spinning of the sample. Centrifugation at the magic angle was performed at a spinning frequency of 8 kHz. ^{29}Si CP MAS NMR spectra were recorded at pulse duration as high as 4.5 μs, contact time equal to 1.5 ms, and pulse spacing 6 s. The ^{13}C CP MAS NMR spectra were recorded at 100.63 MHz in a standard 4 mm MAS probe

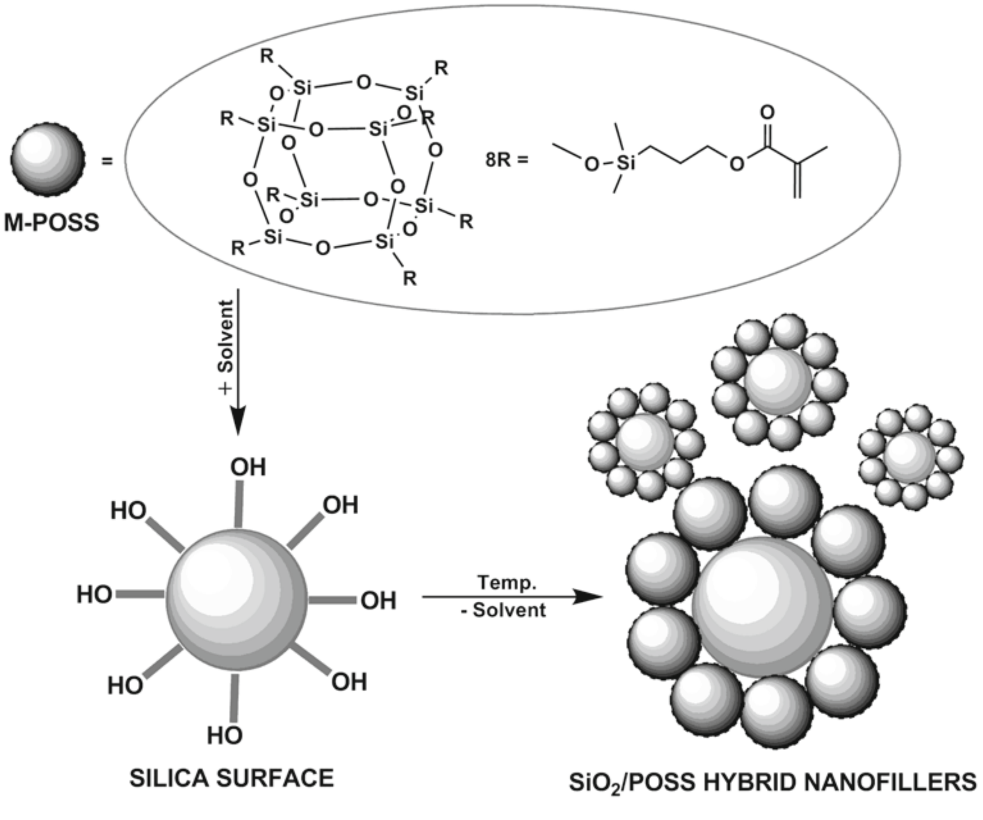

Figure 2. A scheme of interactions between silica and oligosilsesquioxane (M-POSS)

using a single pulse excitation with high power proton decoupling (pulse repetition 10 s, spinning speed 8 kHz).

The surface area S_{BET} (calculated from the BET equation) was measured by low-temperature adsorption of nitrogen. The isotherms of nitrogen adsorption/desorption were measured at 77 K using an ASAP 2020 apparatus (Micromeritics Instrument Co.). On the basis of the isotherms the BET surface area (S_{BET}) was calculated and the pore size (D_P) and volume (V_P) were found from the BJH (Barrett-Joyner-Halenda) equation. With regard to the high accuracy of the instrument used (± 0.0001 m^2/g), the number of surface area values, and the mean pore size (D_P) were rounded off to whole numbers, while the total pore volume (V_P) to two decimal places.

The particle size distributions of the samples were measured using Zetasizer Nano ZS and Mastersizer 2000, both made by Malvern Instruments Ltd., enabling measurements in the range 0.6–6000 nm (NIBS – Non--Invasive Back-scatter method) and 0.2–2000 μm (laser diffraction technique).

The morphology and microstructure of the hybrids obtained was analysed using a Jeol 1200 EX II transmission electron microscope, at an accelerating voltage of 30 kV. The microphotographs were taken using a direct reflection method, which involves covering a net with the formware foil, and then with a thin layer of carbon. On the surface prepared in this way, powder from the suspension was introduced. All samples of the prepared systems were tested in analogous electron conditions.

RESULTS AND DISCUSSION

FTIR, ^{29}Si and ^{13}C CP MAS NMR analysis

Figures 3a and 3b show the FTIR spectra of the unmodified silica supports (HS and ES), and the hybrid systems produced using 10 weight parts by mass of M-POSS. Significant changes were evaluated on the effectiveness of the modification, and on the chemical nature of the silica surface.

The spectra of hydrated and emulsion silica (HS and ES) present two characteristic absorption bands at 1100 and 595 cm^{-1}, which are assigned to Si–O–Si stretching and bending vibration, respectively. The spectrum of unmodified silica also shows an absorption peak at 1640 cm^{-1}, which is assigned to the bending mode of physically absorbed water molecules, in analogy to[32]. By the way, the intensity of the band at 3600–3200 cm^{-1}, assigned to the stretching vibrations of –OH groups coming from physically absorbed water.

The spectra of functionalized samples (HS-10 M-POSS and ES-10 M-POSS) were observed to reduce the intensity of absorption bands assigned to –OH groups in the range of 3600–3200 cm^{-1}. Reduction of the intensity of this band confirms chemical bonding of the modifier to silica surface and effective substitution of double vicinal groups by its molecules. The band at 1720 cm^{-1} arises from the carbonyl stretching vibrations ($\upsilon(=C=O)$). The presence of a weak absorption band at 1550 cm^{-1}, probably related to $\upsilon(C=C)$ also has to be mentioned.

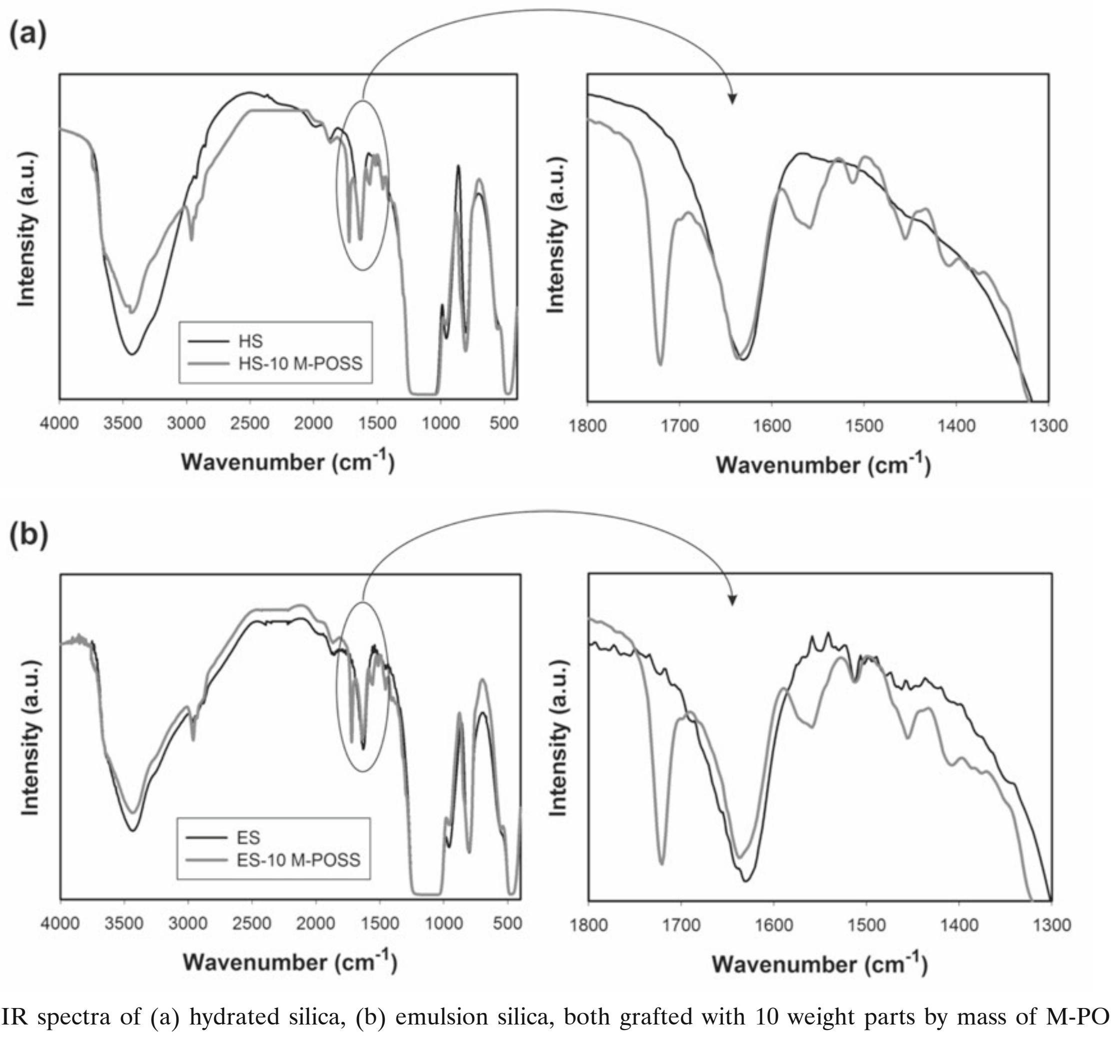

Figure 3. FTIR spectra of (a) hydrated silica, (b) emulsion silica, both grafted with 10 weight parts by mass of M-POSS

Besides, the spectrum of the hybrids produced shows a stretching vibration band υ(C–H) in the range of 2950–2850 cm^{-1}.

The ^{29}Si and ^{13}C CP MAS NMR spectra of hydrated silica (HS) and silica modified with 5 weight parts by mass of octakis({3-methacryloxypropyl}dimethylsiloxy) octasilsesquioxane (HS-5 M-POSS) are presented in Figure 4a and 4b.

The ^{29}Si CP MAS NMR spectrum of the unmodified hydrated silica shows two signals at -110, -100 ppm. The main signal at -100 ppm is assigned to the structure of three siloxane groups and one silanol group – isolated silanols (Q_3), while the signal at -110 ppm – to siloxane bridges (Q_4). After silica surface treatment with M-POSS, the intensities of the Q signals change. This could be caused by the reaction of the methacrylate groups with the surface silanol groups. This reaction will also result in the loss of ≡Si−OH groups and the formation of ≡Si−O−Si≡ linkages. In the spectrum of silica after the modification process, two signals were observed, at -57 ppm and -25 ppm. The first one is assigned to T^2 group (–57 ppm), where T^2 stands for $R_2Si(O_{0,5})_2$ [3, 34]. The structure of this signal brings information of condensation of two or three functional groups on the silica surface. The next signal at -25 ppm most probably corresponds to the unit M of a general formula $R_3SiO_{0,5}$ and different siloxane structures formed[34, 35].

Another evidence of the chemical and physical interactions of the modifiers is given by the ^{13}C CP MAS NMR spectrum presented in Figure 4b. The signals from the range 8 ppm to 21 ppm correspond to the carbon from the hydrocarbon chain ($(–CH_2–)_n$). The signal appearing at 65 ppm is assigned to the carbon from $–OCH_2$ groups. Moreover, a signal at 125 ppm assigned to the $=C=CH_2$ group was observed.

Figure 5 presents the ^{29}Si and ^{13}C CP MAS NMR spectra of emulsion silica (ES) and silica modified with 5 weight parts by mass of octakis({3-methacryloxypropyl}dimethylsiloxy) octasilsesquioxane (ES-5 M-POSS). The spectrum of unmodified emulsion silica (ES) reveals two characteristic signals at -110 ppm and -100 ppm. The spectrum of sample ES-5 M-POSS (modified 5 weight parts by mass of M-POSS) shows additionally the T^3 structure (-94 ppm), probably of condensation of the modifier (M-POSS) with the silica support. As a result of silica functionalization, there is a change in the intensity of signals corresponding to the silanol (Q_3, – 100 ppm) and siloxane groups (Q_4, -110 ppm), which could indicate that chemical interactions have taken place. However, because of the lack of T^2 structure, we can conclude only about the strong adhesion of cage POSS to the silica surface.

In addition a ^{13}C CP MAS NMR spectrum was obtained for the hybrid produced by functionalization of emulsion silica with 5 weight parts by mass of M-POSS. The results are shown in Figure 5b. The signals in the range from 1 to 25 ppm correspond to $–CH_2–$ groups originating from the groups present in the substituents of the modifier. A signal of significant intensity at a chemical shift of 66 ppm is attributed to $–OCH_2$ groups. Moreover, the signals at 209 ppm and 259 ppm are assigned to the $=C=O$ groups, which unfortunately are not clearly visible in the FTIR spectra.

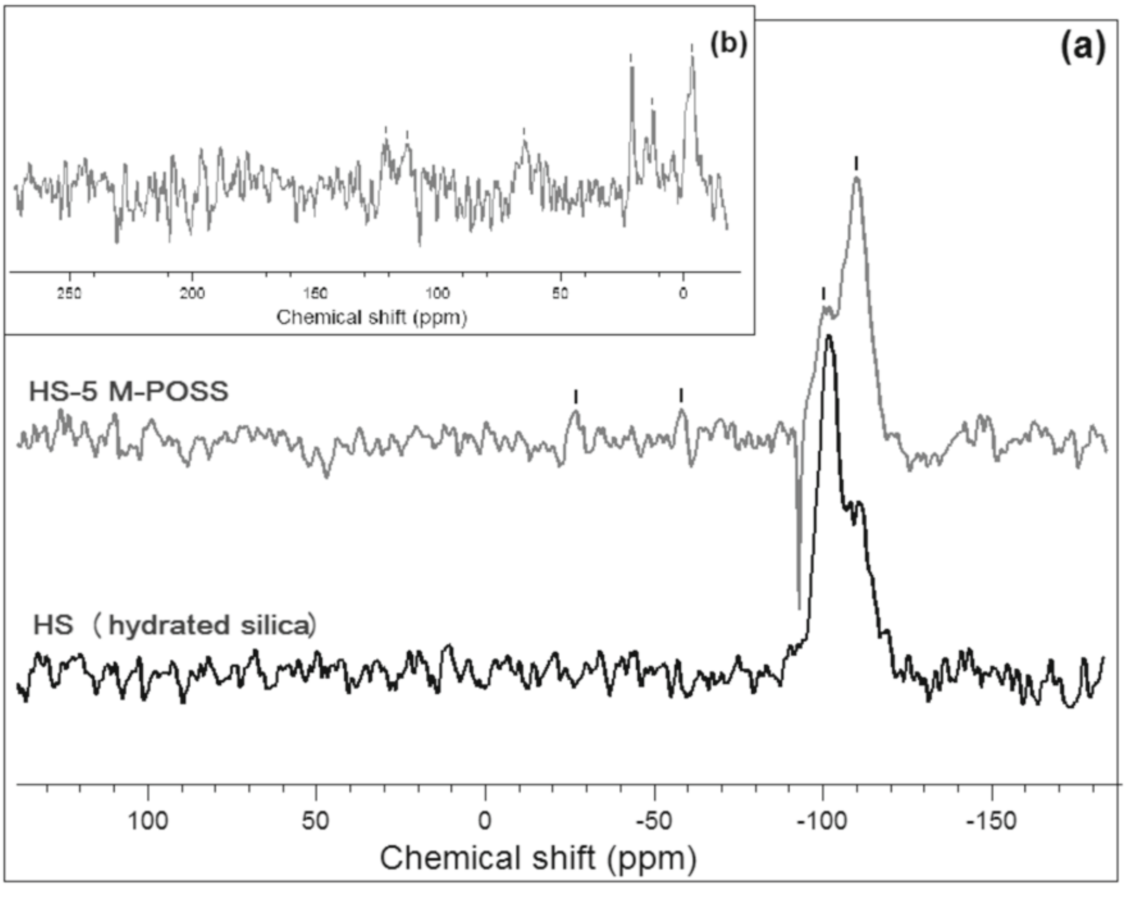

Figure 4. (a) The ^{29}Si CP MAS NMR spectra of unmodified hydrated silica (HS) and SiO_2 functionalized with M-POSS (HS-5 M-POSS), and (b) ^{13}C CP MAS NMR spectrum of HS-5 M-POSS

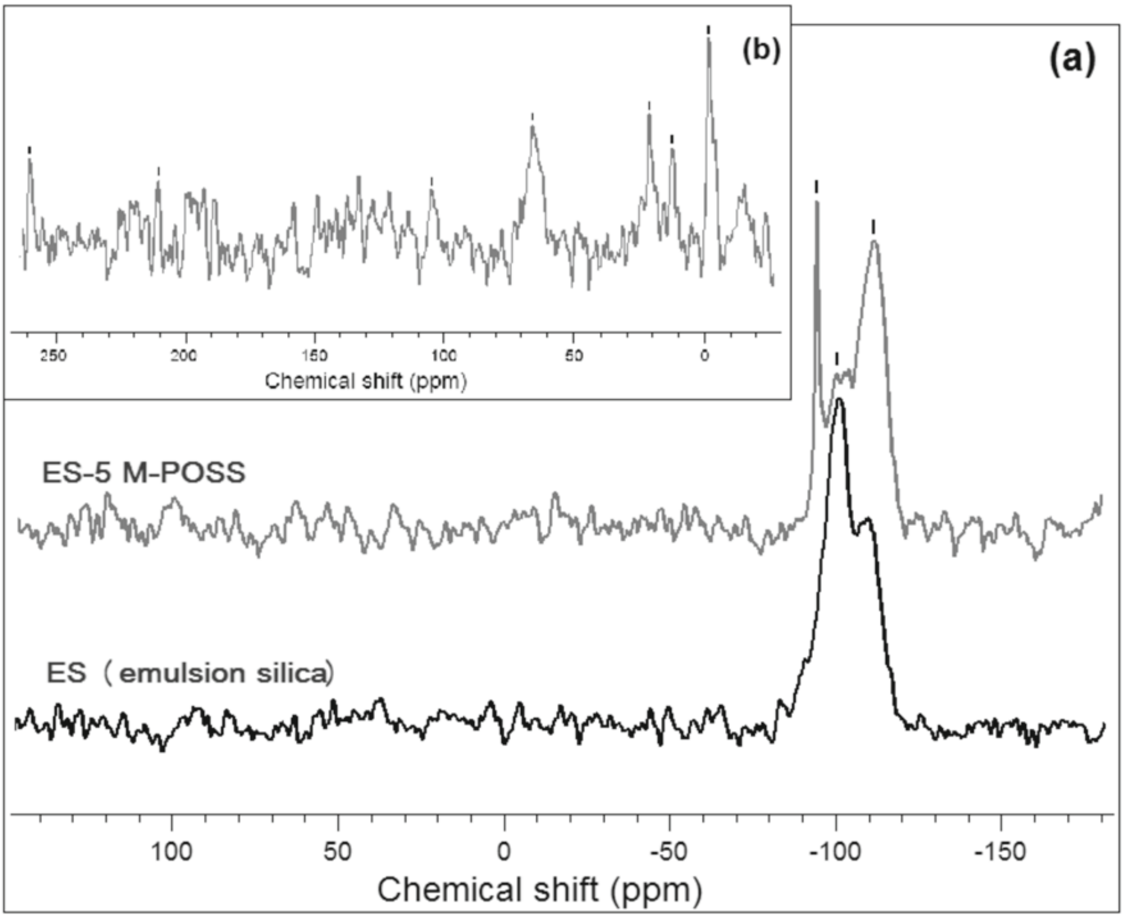

Figure 5. (a) The ^{29}Si CP MAS NMR spectra of unmodified emulsion silica (ES) and SiO_2 functionalized with M-POSS (ES-5 M-POSS), and (b) ^{13}C CP MAS NMR spectrum of ES-5 M-POSS

Description of obtained unmodified silicas and SiO_2/POSS nanofillers porous structure

At the next stage of the study, parameters of porous structure of modified SiO_2 samples were characterized. The fundamental parameters determining the surface activity of the modified samples are surface area (S_{BET}), total pore volume (V_P) and mean diameter of pores (D_P). In addition, Figure 6 shows nitrogen adsorption/desorption isotherms for the initial silica supports (HS and ES) and for the hybrid nanofillers produced.

It was observed that the amount of adsorbed nitrogen on the surface of pure hydrated silica (Fig. 6a) increases until a relative pressure p/p_0 of 0.8 is reached. Above this pressure there is a rapid increase in the quantity of nitrogen adsorbed by HS, to a maximum of 250 cm^3/g at p/p_0 = 0.99. For the systems produced from hydrated silica functionalized with octakis({3-methacryloxypropyl}dimethylsiloxy) octasilsesquioxane (M-POSS), there was a gentler increase in the volume of adsorbed nitrogen after the threshold value was exceeded, and also the maximum values were much lower. As a result of modification of silica with 10 weight parts by mass of M-POSS observed, that a value of the amount of adsorbed nitrogen is equal to 50 cm^3/g at p/p_0 = 0.99 (see Fig. 6a). Also the key parameters indicating the structure of supports and resulting hybrids showed that the surface area S_{BET} of HS was relatively large at 110 m^2/g, while that of the hybrid HS-10 M-POSS was roughly 27 m^2/g (see Table 1). As a result of modification, the pore diameters were found to increase from 13 nm to 23 nm, while the pore volume decreased – the values obtained for the initial sample (HS) and the samples modified with 3, 5 or 10 weight parts by mass of M-POSS were 0.37 cm^3/g, 0.31 cm^3/g, 0.30 cm^3/g and 0.30 cm^3/g, respectively.

Figure 6a presents the nitrogen adsorption/desorption isotherms for the unmodified emulsion silica (ES) and for the hybrids modified with 3, 5 or 10 weight parts by mass of M-POSS. The isotherms show a systematic decrease in the volume of adsorbed nitrogen with increasing relative pressure till reaching a maximum value of 110 cm^3/g for unmodified emulsion silica (ES) at p/p_0 = 0.99 (Fig. 6b). For hybrid nanofillers the increase in

Table 1. Parameters of porous structures of hydrated and emulsion silicas, and hybrids obtained using different amounts of M-POSS

Acronym	S_{BET} (m^2/g)	V_P (cm^3/g)	D_P (nm)
HS	110	0.37	13
HS-3 M-POSS	40	0.31	15
HS-5 M-POSS	39	0.30	19
HS-10 M-POSS	27	0.30	23
ES	40	0.17	16
ES-3 M-POSS	26	0.12	18
ES-5 M-POSS	19	0.10	21
ES-10 M-POSS	8	0.10	22

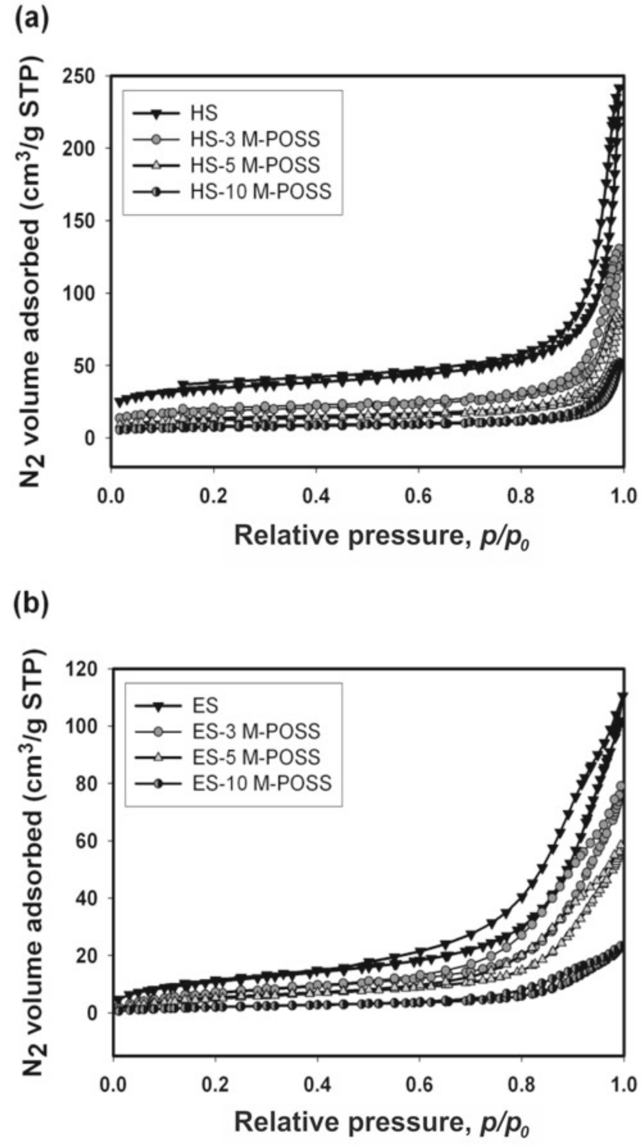

Figure 6. Nitrogen adsorption/desorption isotherms for unmodified hydrated silica (HS), emulsion silica (ES), and both grafted with 3, 5 or 10 weight parts by mass of M-POSS

the volume of adsorbed nitrogen after the threshold value ($p/p_0 = 0.7$) is not so steep and the maximum values for $p/p_0 = 0.99$ are much lower. Also the surface area, and pore volume were significantly lower than those for unmodified silica sample whose S_{BET} was 40 m^2/g. For the sample modified with 10 weight parts by mass of M-POSS (ES-10 M-POSS) the surface area was 8 m^2/g (see Table 1). These changes are a consequence of blocking the active centres on the SiO_2 surface by the molecules of silsesquioxane.

Dispersive and morphological properties of the fillers obtained

The hybrids obtained were subjected to particle size determination to check a possible relation between the degree of agglomeration and the amount of modifier used. Moreover, the unmodified silicas and the hybrid nanofillers were subjected to TEM microphotographs.

Analysis of Table 2 data for the hybrids made with HS has revealed that sample HS-5 M-POSS, obtained with 5 weight parts by mass of M-POSS shows the lowest degree of agglomeration in comparison to unmodified hydrated silica. Moreover, the polydispersity index for this sample is equal to 0.676. As follows from TEM images presented in Figure 7 and the sample parameters from Table 2, the sample modified with 5 weight parts by mass of octakis({3-methacryloxypropyl}dimethylsiloxy) octasilsesquioxane has the maximum volume contribution of particles of diameters smaller than those in the samples modified with 3 or 10 weight parts by mass of M-POSS. The particle size distribution measured for sample HS-5 M-POSS shows only one band covering the particle diameters from the range 190–531 nm. The greatest tendency towards agglomeration was noted for sample HS-10 M-POSS, which is related to the use of the greatest amount of the modifier for its preparation.

The size of particles in samples synthesized on the basis of hydrated silica was measured by Mastersizer 2000 (Table 2). In sample HS-5 M-POSS obtained with 5 weight parts by mass of M-POSS 10% of particles had diameters not greater than 15.11 μm, 50% of particles had diameters not greater than 38.85 μm and 90% not greater than 93.71 μm. The mean diameter of particles in this sample D[4.3] corresponded to agglomerations of the maximum diameter of 26.08 μm. TEM images of samples obtained with 3, 5 and 10 weight parts by mass of M-POSS (Fig. 7) inform about their inhomogeneous structure and the presence of primary particles and secondary agglomerates. Particles of irregular shapes making larger clusters are observed for samples of unmodified silica support, HS-3 M-POSS, and HS-10 M-POSS (Figs. 7a, 7b, 7d). HS-5 M-POSS (Fig. 7c) has the particles of the greatest refinement, they are much smaller and the clusters they make are also small.

The hybrid nanofillers obtained by functionalization of emulsion silica (ES) with M-POSS show a much different dispersive and morphological character. The relevant data are presented in Table 3. Because of significant hydrophobicity of these samples, no measurements of particle size distribution by the laser diffraction method were made.

As follows from these data, sample ES-3 M-POSS (emulsion silica modified with 3 weight parts by mass

Table 2. Dispersion properties of the hybrid nanofillers made of hydrated silica (HS) and octakis({3-methacryloxypropyl}dimethylsiloxy) octasilsesquioxane (M-POSS)

Acronym	Amount of POSS (weight parts by mass)	Zetasizer Nano ZS			Mastersizer 2000			
					Particles size (µm)			
		diameters range (nm)	dominant particles diameter (nm)	PdI index	d(0.1)	d(0.5)	d(0.9)	D[4.3]
HS	–	164–531	255 (18.8%)	0.744	5.91	15.40	30.64	17.18
HS-3 M-POSS	3	91–164	396 (22.3%)	0.732	8.96	43.30	78.67	36.21
HS-5 M-POSS	5	190–531	255 (26.4%)	0.676	15.11	38.85	93.71	26.08
HS-10 M-POSS	10	106–190; 4150–6440	5560 (29.3%)	0.739	13.05	42.51	98.50	39.09

Table 3. Dispersion properties of hybrid nanofillers made of emulsion silica and octakis({3-methacryloxypropyl}dimethylsiloxy) octasilsesquioxane (M-POSS)

Acronym	Amount of POSS (weight parts by mass)	Zetasizer Nano ZS		
		diameters range (nm)	dominant particles diameter (nm)	PdI
ES	–	255–712	396 (34.7%)	0.252
ES-3 M-POSS	3	255–712	396 (28.6%)	0.212
ES-5 M-POSS	5	255–1280	825 (19.3%)	0.371
ES-10 M-POSS	10	396–955	615 (28.5%)	0.240

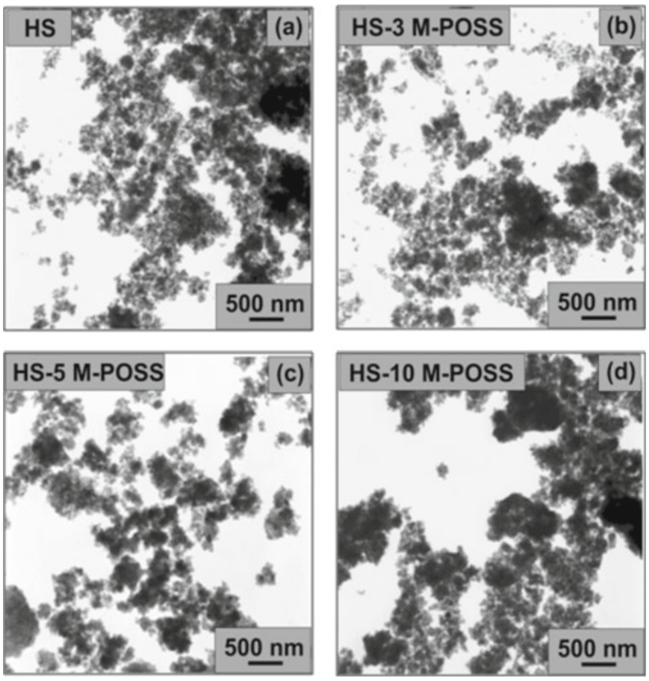

Figure 7. TEM microphotographs of (a) pure hydrated silica and hybrids modified with (b) 3, (c) 5, and (d) 10 weight parts by mass of octakis({3-methacryloxypropyl}dimethylsiloxy) octasilsesquioxane (M-POSS)

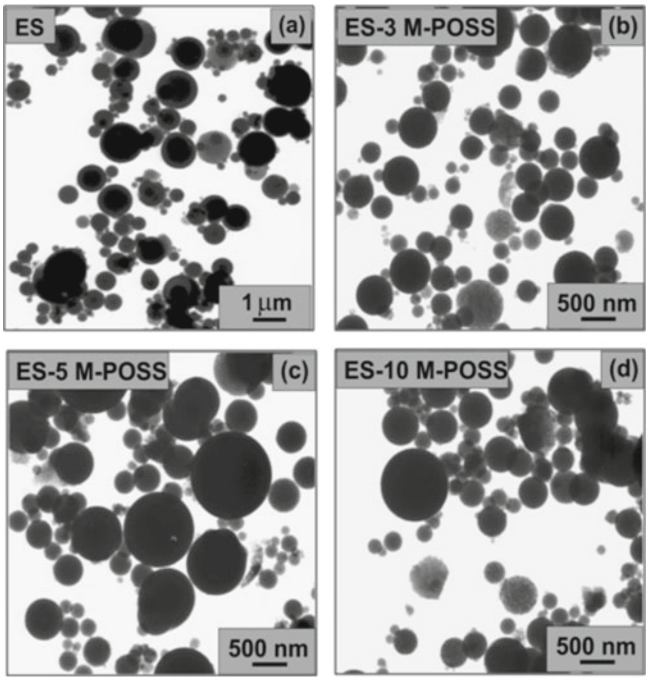

Figure 8. TEM microphotographs of (a) pure emulsion silica and hybrids modified with (b) 3, (c) 5, and (d) 10 weight parts by mass of octakis({3-methacryloxypropyl}dimethylsiloxy) octasilsesquioxane (M-POSS)

M-POSS) is characterized by the greatest degree of homogeneity, which is confirmed by the particle size distribution measured by Zetasizer Nano ZS. The polydispersity index of this sample is equal to 0.212. The sample obtained with 5 weight parts by mass of M-POSS also shows the lowest tendency towards agglomeration (Fig. 8b). Its particles have spherical shape and their adhesion to irregular M-POSS particles is rather strong. The polydispersity index characterizing the other samples is somewhat higher (see Table 3). The hybrid samples obtained with 5 and 10 weight parts by mass of octakis({3-methacryloxypropyl}dimethylsiloxy) octasilsesquioxane are definitely non-homogeneous. The data obtained by Zetasizer Nano ZS measurements are supported by TEM images shown in Figure 8. The unmodified sample (Fig. 8a) and the hybrid samples show particles of spherical shape. The irregular shaded areas evidence the presence of the modifier. For samples ES-5 M-POSS (Fig. 8c) and ES-10 M-POSS (Fig. 8d) the presence of primary and secondary particles is particularly pronounced.

CONCLUSIONS

The proposed process of SiO_2 modification with a POSS compound based on solvent evaporation is a relatively simple method which could be widely used. The chemistry of the functionalization reaction was investigated by FTIR and ^{29}Si and ^{13}C CP MAS NMR. The FTIR spectra permitted identification of particular functional groups of the modifier present in the SiO_2/POSS hybrid systems obtained. The proposed method of modification ensured effective change of the physicochemical parameters of prepared silica supports. NMR analysis confirmed the effectiveness of modification in the process proposed.

Based on porous structure parameters reduction of values of BET surface area and total pore volume (V_P) has been notified. In the same time, the mean diameter of pores (D_P) increased. The amount of nitrogen adsorbed decreased in direct proportion to the increasing content of POSS modifier. This effect results from the blocking of active sites on the SiO_2 surface by molecules of the modifier.

As a result of modification of silica support with a chosen cage POSS (M-POSS) a change was also observed in the dispersive character of the samples. No direct correlations were found between the dispersive properties of the hybrid samples obtained and the amount of the modifier used (3, 5 or 10 weight parts by mass of SiO_2) and a possible increase in agglomeration.

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