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Immobilization of multifunctional silsesquioxane cage on precipitated silica supports

K. Szwarc-Rzepka · B. Marciniec · T. Jesionowski

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Abstract Synthesis of octakis({3-glycidoxypropyl}dimethylsiloxy) octasilsesquioxane (G-POSS) was carried out based on a reaction involving the hydrosilylation of allyl glycidyl ether with octakis(dimethylsiloxy) octasilsesquioxane, using Karstedt's catalyst and toluene. SiO_2/POSS hybrid systems were obtained via a method of immobilization by evaporation of the solvent, using hydrated or spherical silica obtained by precipitation in an aqueous or emulsion environment. The surface of the SiO_2 was modified using octakis({3-glycidoxypropyl}dimethylsiloxy) octasilsesquioxane (G-POSS). The effectiveness of the modification of the obtained hybrid materials was verified using Fourier transform infrared spectroscopy and nuclear magnetic resonance (^{29}Si and ^{13}C CP MAS NMR). The tests showed that the interactions between the silica support and the modifier are of the nature of chemical adsorption. In addition a mechanism was proposed for the interactions between silica and oligosilsesquioxane. To test the final effect, the hybrid systems were subjected to morphological evaluation (transmission electron microscopy). Parameters of porous structure of the products were also determined: the specific surface area, pore diameter and pore volume. Thermal stability was tested for the pure silsesquioxane cage, the initial silica supports and the resulting systems. Elemental analysis was also carried out to determine the effect of surface modification on the degree of coverage with a particular POSS compound.

Keywords: Multifunctional silsesquioxane cage · Silica · Immobilization · Functionalization · Chemisorption

1 Introduction

Hybrid nanomaterials are systems produced from the combining of organic or inorganic particles or materials containing both organic and inorganic centres (Thostenson et al. 2005) where, according to the EU Commission recommendation on the definition of nanomaterials (2011/696/EU), one or more external dimensions is in the size range between 1 and 100 nm. Polyhedral oligomeric silsesquioxanes (POSS) are classified as 3D nanofillers (Goffin et al. 2007) and are characterized by a closed organic–inorganic cage structure (Zhang et al. 2007). Oligosilsesquioxanes are successfully used to make new hybrid nanocomposites, which have already proven useful in many applications, including in the formation of insulating layers (Baney et al. 1995), in the preparation of dental fillings (Fong et al. 2005), and in polymer processing (Wheeler et al. 2006; Mammeri et al. 2009; Sarantopoulou et al. 2009; Qin et al. 2010; Lin et al. 2009). POSS nanostructures can be incorporated into the polymer matrix by means of copolymerization, grafting or mixing, thus enabling the preparation of new thermosetting or thermoplastic materials (Chiu et al. 2010; Blanco et al. 2012).

Octakis({3-glycidoxypropyl}dimethylsiloxy) octasilsesquioxane is an attractive compound in view of its reactive substituents, which undergo polymerization easily in spite of their highly developed structure (Zhang and Laine 1996). For this reason, POSS with epoxide groups has been the subject of numerous studies. For example, Lee and Litchtenhan (1998)

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used macromers of epoxide POSS in reaction with diglycidyl ether of bisphenol-A in order to change the vitrification temperature. Liu et al. (2005) used octaepoxy-POSS to improve epoxy curing reactivity as well as cross-linking density. In turn, Choi et al. (2001) investigated the effect of octasilsesquioxanes, with (among others) dimethylsiloxypropylglycidyl groups, on epoxy resin. They found that the dynamic mechanical properties, fracture toughness and thermal stability are strongly dependent on the type of R side groups occurring in the cage corners. As a result of attachment of the POSS cage to the epoxide matrix, defects were observed in the silsesquioxane cage structure.

Nanoporous materials such as activated carbons, zeolites, silica gels and others play an important role in science and technology, particularly in adsorption, catalysis, separation and purification (Grudzien et al. 2007). Much attention has been paid recently to the preparation of nanomaterials with precisely designed surfaces and structural properties (Choma et al. 2009).

Silica (SiO_2) is among the most commonly used fillers, of which parameters such as bulk density, tap density and specific surface area depend significantly on the method used and the technological parameters (Jesionowski 2002; Żurawska et al. 2003; Bula et al. 2007). SiO_2 differs somewhat from the silsesquioxanes. It is an unordered material, but still its susceptibility to chemical modifications is excellent (Jesionowski et al. 2010). In addition, silanol groups are present on the surface of the silica or in the internal structure—these provide the compound's high level of activity (Bergna and Roberts 2006; Georgakilas et al. 2008). In view of these excellent properties of silica, and the high degree of incorporation of epoxide groups into the SiO_2 surface, it was decided to combine it with POSS, and hybrid systems with unchanged properties relative to the initial compounds were produced (Szwarc-Rzepka et al. 2012). This is an alternative to traditional fillers, and leads to the development of organic–inorganic hybrid materials. They combine the advantageous features of inorganic materials, such as high thermal stability and mechanical strength, with those of organic materials, for example elasticity (Kawakami 2007; Rios et al. 2011).

The purpose of the present work was to develop a new generation of hybrid systems, to be used, among other things, as polymer fillers, and also as adsorbents or heterogeneous catalysts. Only a few studies have been carried out to date on materials of this type (Carniato et al. 2008; Szwarc-Rzepka et al. 2012; Ambrozewicz et al. 2012).

2 Experimental

2.1 Synthesis of octakis({3-glycidoxypropyl}dimethylsiloxy) octasilsesquioxane

Octakis({3-glycidoxypropyl}dimethylsiloxy) octasilsesquioxane (G-POSS) was synthesized according to the two-stage process published elsewhere (Filho et al. 2006; Jeziorska et al. 2011). The POSS was obtained in a process based on a reaction involving the hydrosilylation of allyl glycidyl ether (AGE) with octakis(dimethylsiloxy) octasilsesquioxane. The reaction was carried out in an open system in an environment of toluene solvent with the use of Karstedt's catalyst in a quantity of 1×10^{-5} mol Pt/mol Si–H. POSS solution and AGE were placed in a flask in molar ratio 1:1.2, into which the catalyst was added. The mixture was heated at 100 °C for 6 h. Afterwards, the toluene and excess AGE were removed through evaporation. Tetraethoxysilane, AGE and toluene are of chemically pure grade, and were purchased from Sigma Aldrich. The method of synthesis of G-POSS is shown schematically in Fig. 1.

2.2 Preparation of SiO_2/POSS hybrids

The process began with the formation of silicas on a large laboratory scale. Two types of silica were prepared: obtained in an aqueous (hydrated silica) or polar (emulsion silica) system. The concept of the production of the silica

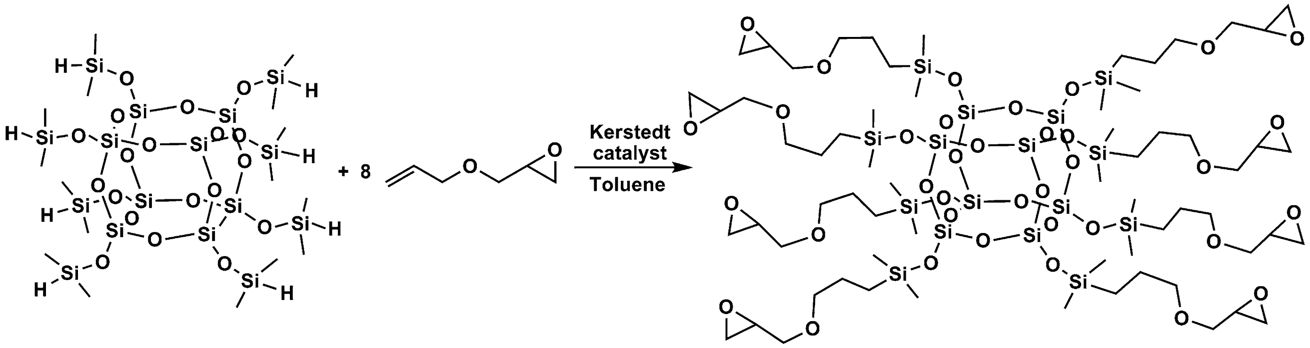

Fig. 1 Synthesis of octakis({3-glycidoxypropyl}dimethylsiloxy) octasilsesquioxane

support is described in detail by Jesionowski et al. (2003), Jesionowski (2009).

SiO_2/POSS hybrid systems were obtained via a method of immobilization by evaporation of the solvent. Firstly, the previously prepared fraction of hydrated or emulsion silica was placed in a reactor, into which a mixture of glycidoxy-POSS compound and toluene was introduced by atomization. The modifying agent was introduced in 3, 5 or 10 weight parts by mass of the silica support. When atomization was complete, the entire system was transferred to a round-bottomed flask and placed in a vacuum rotary evaporator (Rotavapor RII, Büchi Labortechnik AG), in order to carry out the modification and to remove the solvent (water bath temperature 60 °C, pressure 337 mbar). The final stage consisted of convection drying of the product, performed in a drying chamber at 120 °C for 48 h.

2.3 Evaluation of physicochemical properties

To monitor the course of the synthesis and to verify the products' structure, the spectra ^{1}H NMR (nuclear magnetic resonance, 300 MHz), ^{13}C NMR (75 MHz) and ^{29}Si NMR (59 MHz) were recorded on a Varian XL 300 spectrometer at room temperature, using C_6D_6 as solvent. All chemicals were used as obtained from suppliers without any further purification.

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 flakes. FTIR spectra were obtained in the transmission mode between 4,000 and 400 cm^{-1}.

^{29}Si NMR 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 a 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 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 Brunauer–Emmett–Teller [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 specific 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 surface area values and the mean pore size (D_P) were rounded off to whole numbers, and the total pore volume (V_P) to two decimal places.

The chemical composition of the functionalized SiO_2 systems was determined using a Vario EL Cube apparatus (Elementar Analysensysteme GmbH). A 10 mg portion of the sample was placed in an 80-position autosampler. The sample was placed in a system in which it was combusted in an oxygen atmosphere. After passing through appropriate catalysts in a helium stream, the resulting gases were separated in a chromatography column, and then recorded using a katharometer. The results are given to ±0.001 %, and each is obtained by averaging three measurements.

The morphology and microstructure of the hybrids obtained was analysed using a Jeol 1200 EX II transmission electron microscope, at an accelerating voltage of 80 kV. Microscopic photographs 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

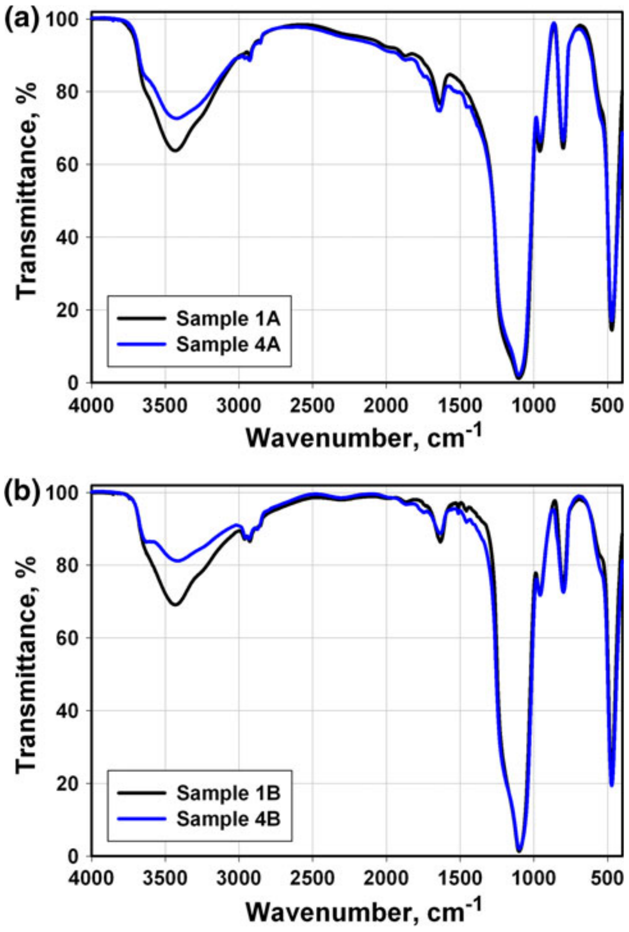

Fig. 2 FTIR spectra of **a** hydrated silica, **b** emulsion silica, both grafted with 10 weight parts by mass of G-POSS

was introduced. All samples of the prepared systems were tested in analogous electron conditions with appropriate magnification.

Thermogravimetric analysis was performed using a Jupiter STA 449F3 (Netzsch GmbH). Samples weighing approximately 10.0 mg were placed in an Al_2O_3 crucible, and heated at a rate of 10 °C/min from 30 to 1,000 °C in a nitrogen atmosphere, at a flow rate equal to 40 cm^3/min.

3 Results and discussion

3.1 Characteristics of octakis({3-glycidoxypropyl}-dimethylsiloxy) octasilsesquioxane

The results of the NMR analysis of the silsesquioxane product confirmed its structure:

^{1}*H NMR* ($CDCl_3$, 298 K, 300 MHz) δ (ppm) = 0.05 ($OSiCH_3$); 0.51 ($SiCH_2$); 1.51 (CH_2); 2.47, 2.65 (CH_2O); 3.00 (CHO); 3.25 (CH_2O); 3.33, 3.56 (OCH_2).

^{13}*C NMR* ($CDCl_3$, 298 K, 75.5 MHz) δ (ppm) = −0.66 ($SiCH_3$); 13.39 ($SiCH_2$); 22.89 (CH_2); 43.98 (CH_2O); 50.29 (CHO); 71.75 (OCH_2); 73.61 (CH_2O).

^{29}*Si NMR* ($CDCl_3$, 298 K, 59.6 MHz) δ (ppm) = 12.87 ($OSi(CH_3)_2$); −109.13 (SiOSi).

FTIR (*ATR*) ν(CH) 3053, 2930, 2868; ν(C–O); 1254 ν(Si–O) 1070; δ(C–O–C) 837 cm^{-1}.

3.2 SiO_2/POSS hybrids

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

Figure 2a, b show the FTIR spectra of the unmodified silica supports (samples 1A and 1B), and of the hybrid systems produced using 10 weight parts by mass of G-POSS. Significant changes were recorded in the effectiveness of the modification, and in the chemical nature of the silica surface.

An analogous situation was observed in the spectra of silica produced from an aqueous system (sample 1A) and from an emulsion system (sample 1B). The spectra showed two characteristic absorption bands at 1,100 and 595 cm^{-1}, attributed to stretching vibrations of ν(Si–O–Si) groups. In turn the absorption band at 1,640 cm^{-1} is attributed to physically absorbed water, analogously as in (Szwarc-Rzepka et al. 2012). Moreover, in the range 3,600–3,200 cm^{-1} wide absorption bands corresponding to

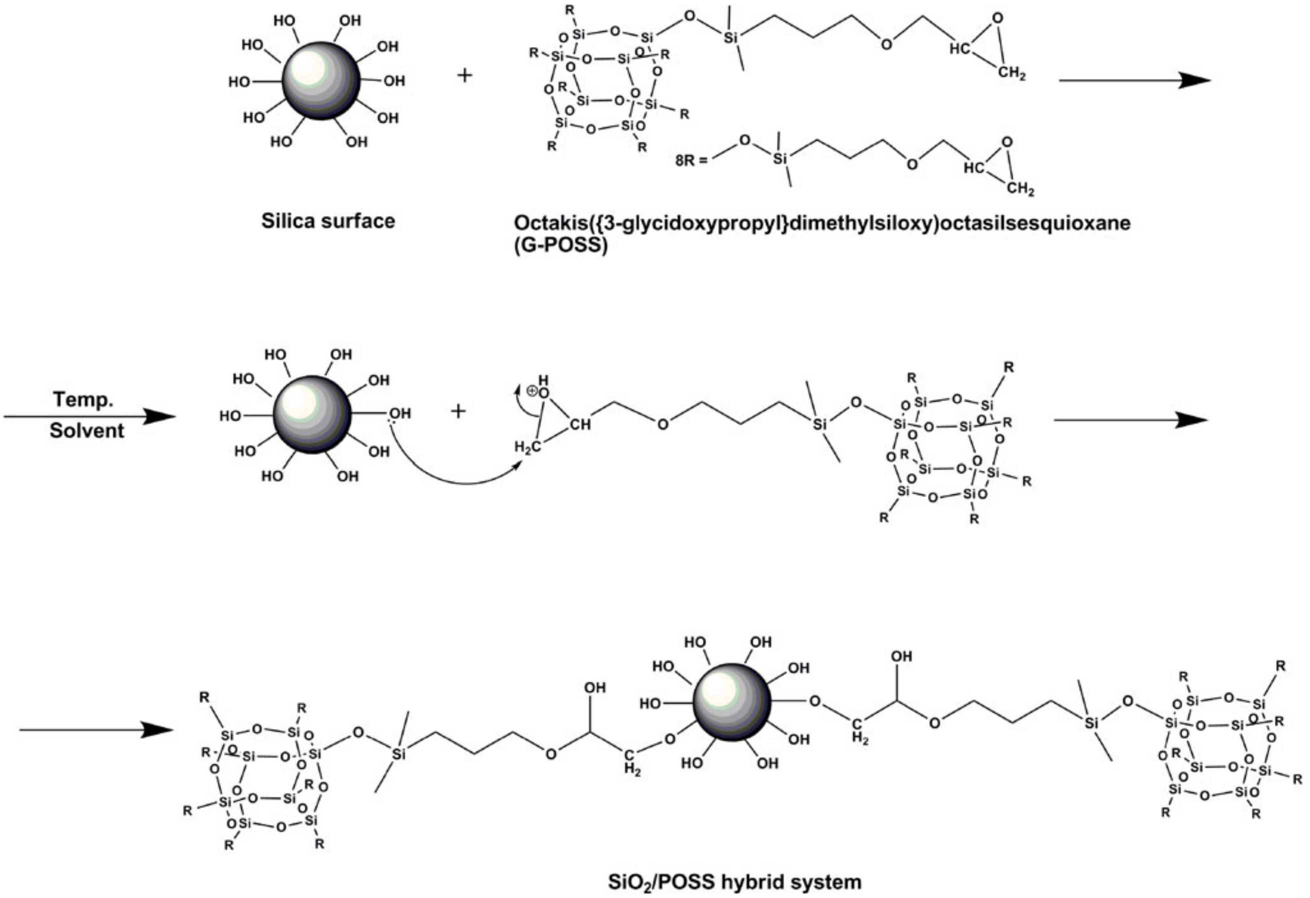

Fig. 3 Predicted mechanism of silica surface functionalization

stretching vibrations of –OH groups were observed. In the case of modified samples of octakis({3-glycidoxypropyl}dimethylsiloxy) octasilsesquioxane, a drop in the intensity of the absorption bands was noted. The decrease in the intensity of this band provides some evidence of the chemical incorporation of the modifier with the silica surface. Also observed on the spectrum of the produced hybrids was a group of *v*(C–H) stretching vibrations in the range 2,900–2,850 cm^{-1}. Also, for the systems made using 10 weight parts by mass of G-POSS, minor absorption bands corresponding to a set of stretching vibrations of Si–C groups in the range 1,400–1,200 cm^{-1} were observed. However in the range 950–750 cm^{-1} the absorption bands characteristic for a closed epoxide ring were not observed, analogously as in (Choi et al. 2001). Figure 3 shows a mechanism for the interactions between silica and oligosilsesquioxane (G-POSS).

The effectiveness of the modification was also verified using the technique of NMR. Figure 4a, b present the ^{29}Si and ^{13}C CP MAS NMR spectra of pure hydrated silica (sample 1A), and of a silica support modified with 5 weight parts by mass of G-POSS (sample 3A).

On the ^{29}Si CP MAS NMR spectrum (Fig. 4a) of unmodified hydrated silica, two characteristic signals are visible. The first main signal, at −100 ppm, is attributed to three siloxane groups and one silanol group (Q_3), while the second signal, at −110 ppm, corresponds to four siloxane bridges (Q_4). As a result of the modification of the silica surface with octakis({3-glycidoxypropyl}dimethylsiloxy) octasilsesquioxane, a change in the intensity of signals Q_3 and Q_4 was observed, along with the appearance of a structure corresponding to the T^3 group at ca. −80 ppm. This provides evidence of chemical grafting of the reactive groups appearing on the silica surface and the reactive epoxide

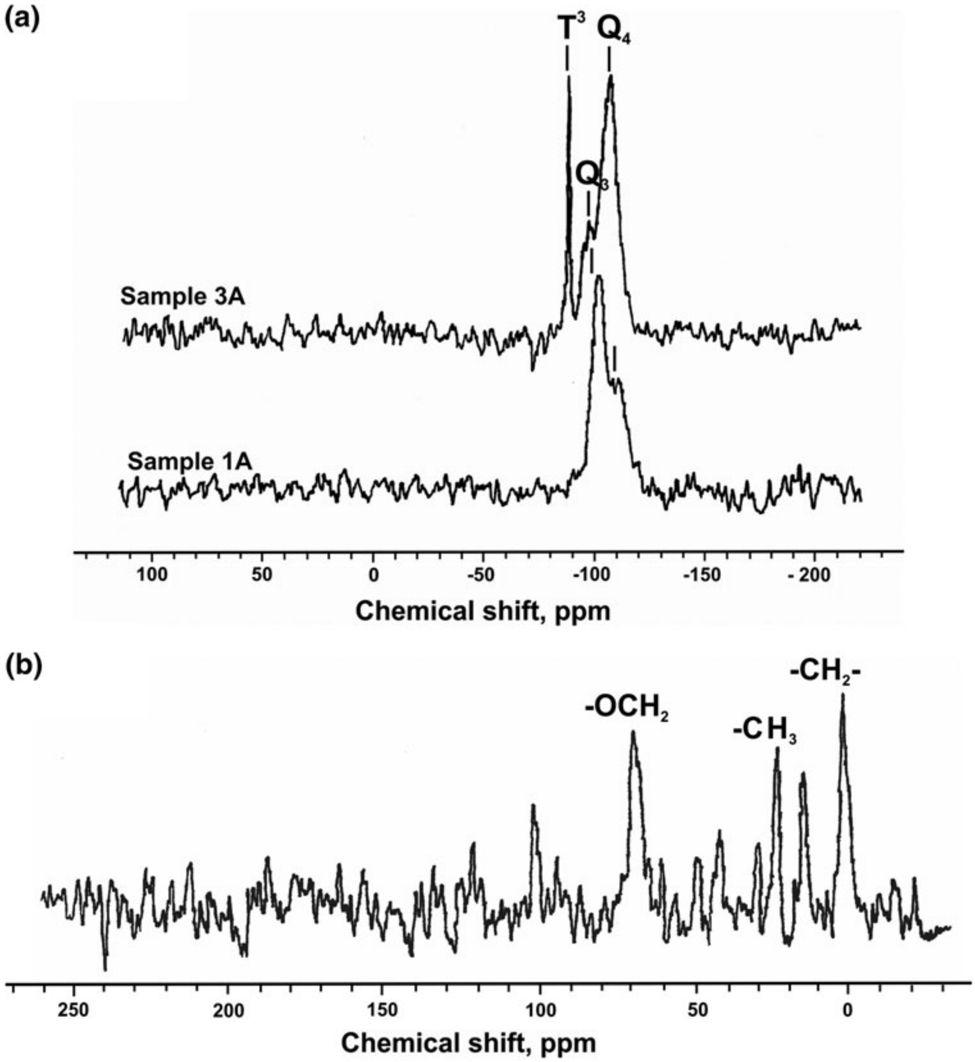

Fig. 4 **a** ^{29}Si CP MAS NMR spectra of unmodified hydrated silica (sample 1A) and SiO_2 functionalized with G-POSS (sample 3A), and **b** ^{13}C CP MAS NMR spectrum of hydrated silica functionalized with octakis({3-glycidoxypropyl}dimethylsiloxy) octasilsesquioxane (sample 3A)

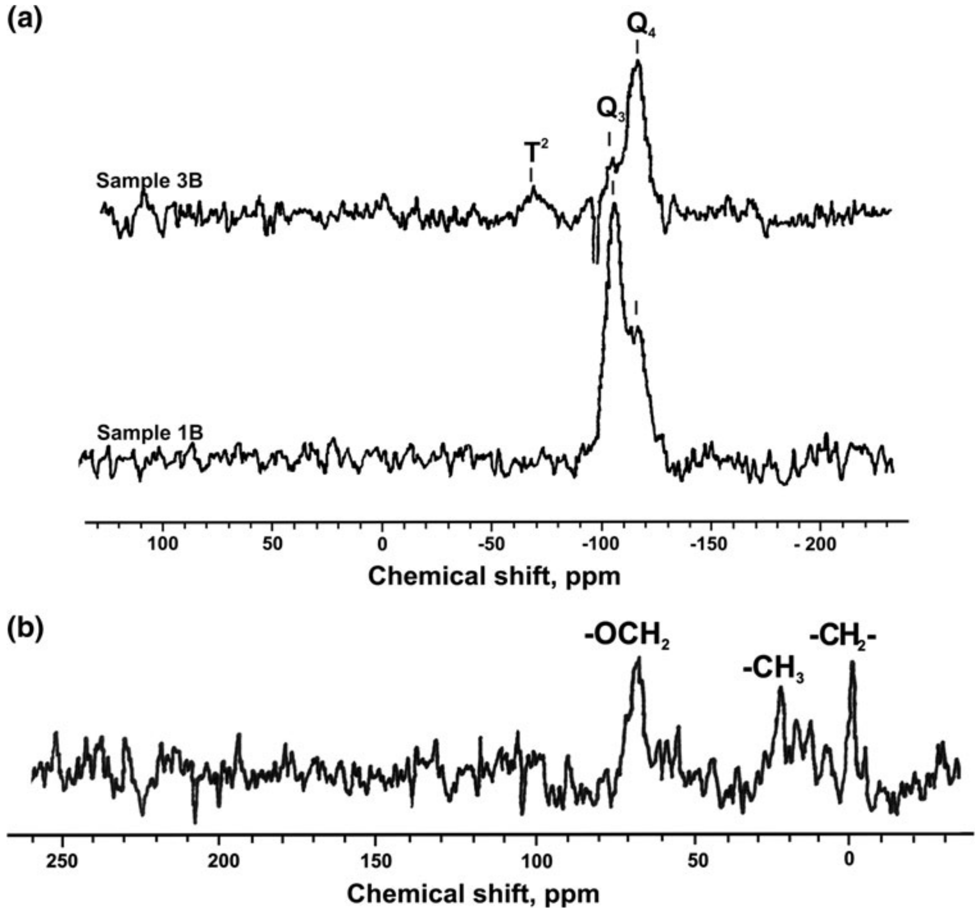

Fig. 5 **a** ^{29}Si CP MAS NMR spectra of unmodified emulsion silica (sample 1B) and SiO_2 grafted with G-POSS (sample 3B), and **b** ^{13}C CP MAS NMR spectrum of emulsion silica functionalized with octakis({3-glycidoxypropyl}dimethylsiloxy) octasilsesquioxane (sample 3B)

groups, which at raised temperatures undergo dissociation, and are easily immobilized on the surface of the silica support.

In addition a ^{13}C CP MAS NMR spectrum was obtained for the hybrid produced by functionalization of hydrated silica with 5 weight parts by mass of G-POSS. The results are shown in Fig. 4b. The signals in the range from 1 to 25 ppm correspond to $–CH_2–$ and $–CH_3$ groups originating from groups present in the substituents of the modifier. A signal of significant intensity at a chemical shift of 69 ppm is attributed to $–OCH_2$ groups.

In turn, Fig. 5a shows the ^{29}Si CP MAS NMR spectra of silica precipitated in an emulsion system (sample 1B), and of a hybrid system functionalized with 5 weight parts by mass of G-POSS (sample 3B). In this case as well, for the unmodified silica support there are two characteristic signals at -100 and -110 ppm. As a result of the functionalization there was a change in the intensity of the signals Q_3 and Q_4, which provides evidence of the effective substitution of silanol groups by molecules of the modifier. Moreover a signal was observed at -67 ppm, corresponding to the T^2 structure (Schütz et al. 2010; Chiang et al. 2003). As a result, it can be assumed that chemisorption occurred in this case as well.

Figure 5b shows the ^{13}C CP MAS NMR spectrum of the hybrid obtained by the functionalization of emulsion silica with 5 weight parts by mass of G-POSS. Analogous signals were observed as in the case of the hybrid produced on hydrated silica. Characteristic signals were also recorded in the range from 1 to 25 ppm, corresponding to $–CH_2–$ and $–CH_3$ groups originating from the hydrocarbon chain present in the substituents of G-POSS. In addition a signal of significant intensity at a chemical shift of 69 ppm was attributed to $–OCH_2$.

The data of the porous structure of the initial compounds and of the hybrid systems were also tested. Table 1 gives the parameters for specific surface area (S_{BET}), pore volume (V_P) and pore diameter (D_P). In addition, Figs. 6 and 7 show nitrogen adsorption/desorption isotherms and pore size for the initial silica supports (samples 1A and 1B) and for the hybrid systems produced.

Based on analysis of the data in Figs. 6 and 7, the character of the curves obtained was found to indicate that the samples had a mesoporous structure. According to the

Table 1 Parameters of the porous structure of hydrated and emulsion silicas and hybrid systems obtained using different quantities of G-POSS

Sample numbers	S_{BET} (m^2/g)	$V_{\mathrm{P}}^{\mathrm{BJH}}$ (cm^3/g)	$D_{\mathrm{P}}^{\mathrm{BJH}}$ (nm)
1A	110	0.37	13
2A	50	0.31	25
3A	42	0.30	33
4A	34	0.30	34
1B	40	0.17	16
2B	25	0.12	16
3B	25	0.12	19
4B	11	0.10	24

IUPAC classification, these are type IV isotherms with a type H3 hysteresis loop, the character of which is associated with capillary condensation in the mesopores. It was observed that the quantity 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. After this pressure is exceeded there is a rapid increase in the quantity of nitrogen adsorbed for sample 1A, reaching a maximum of 250 cm^3/g at $p/p_0 = 1$. For the systems produced from hydrated silica functionalized with octakis({3-glycidoxypropyl}dimethylsiloxy) octasilsesquioxane (G-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 the modification of silica with 10 weight parts by mass of G-POSS, a value of 190 cm^3/g was recorded at $p/p_0 = 1$ (see Fig. 6d). Also the key parameters indicating the structure of the supports and of the resulting hybrid materials showed that the specific surface area value S_{BET} for sample 1A was relatively large at 110 m^2/g, while that for hybrid 4A was roughly 34 m^2/g (Table 1).

A consequence of the decrease in the specific surface area values is certainly the effect of the blocking of active sites on the silica by molecules of the modifier. It was also observed that the modification process caused an increase in pore diameters from 13 to 34 nm. At the same time there was a decrease in pore volume, which for the initial sample and for samples modified with 3, 5 or 10 weight parts by mass of G-POSS was equal to 0.37, 0.31, 30, and 30 cm^3/g respectively.

Analysing the nitrogen adsorption/desorption isotherms and the pore size distributions of emulsion silica and the

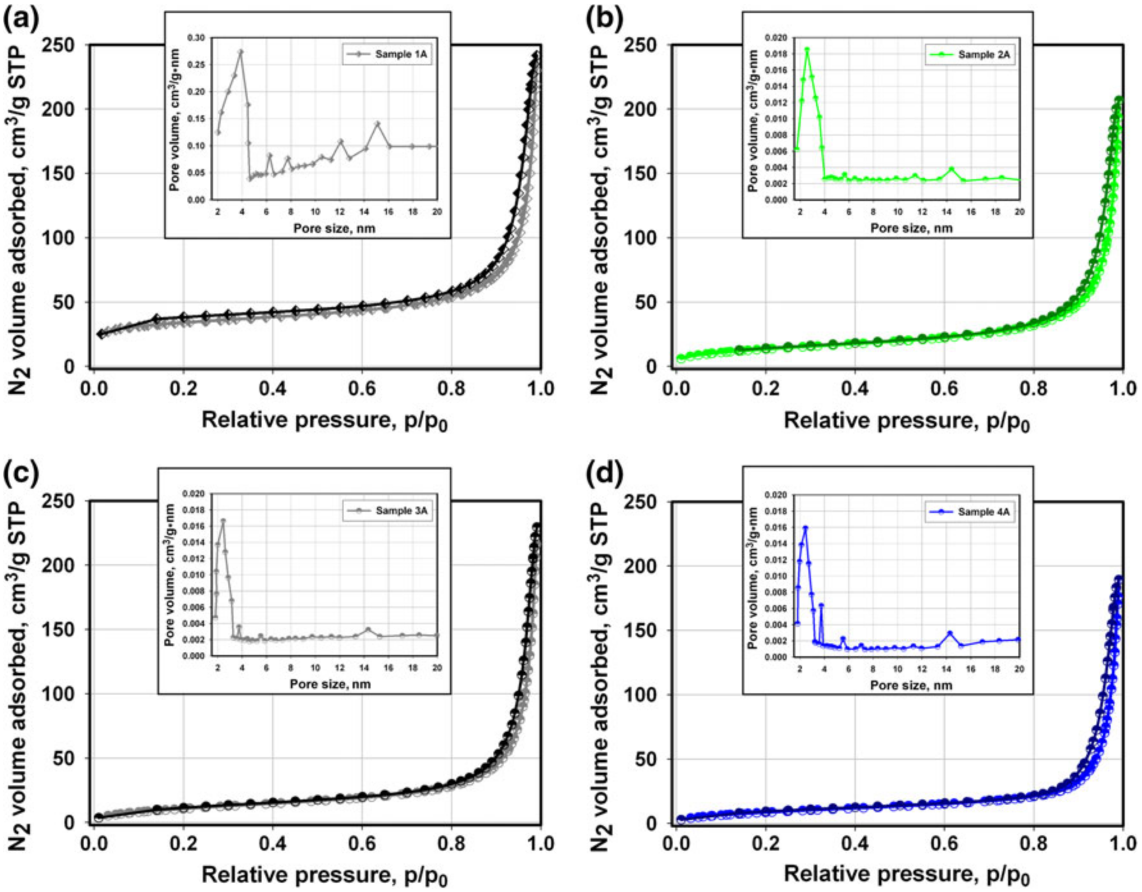

Fig. 6 Nitrogen adsorption/desorption isotherms and pore size distribution for unmodified hydrated silica (sample 1A (**a**)) and hybrid systems obtained using 3, 5 or 10 weight parts by mass of G-POSS (samples 2A (**b**), 3A (**c**), 4A (**d**))

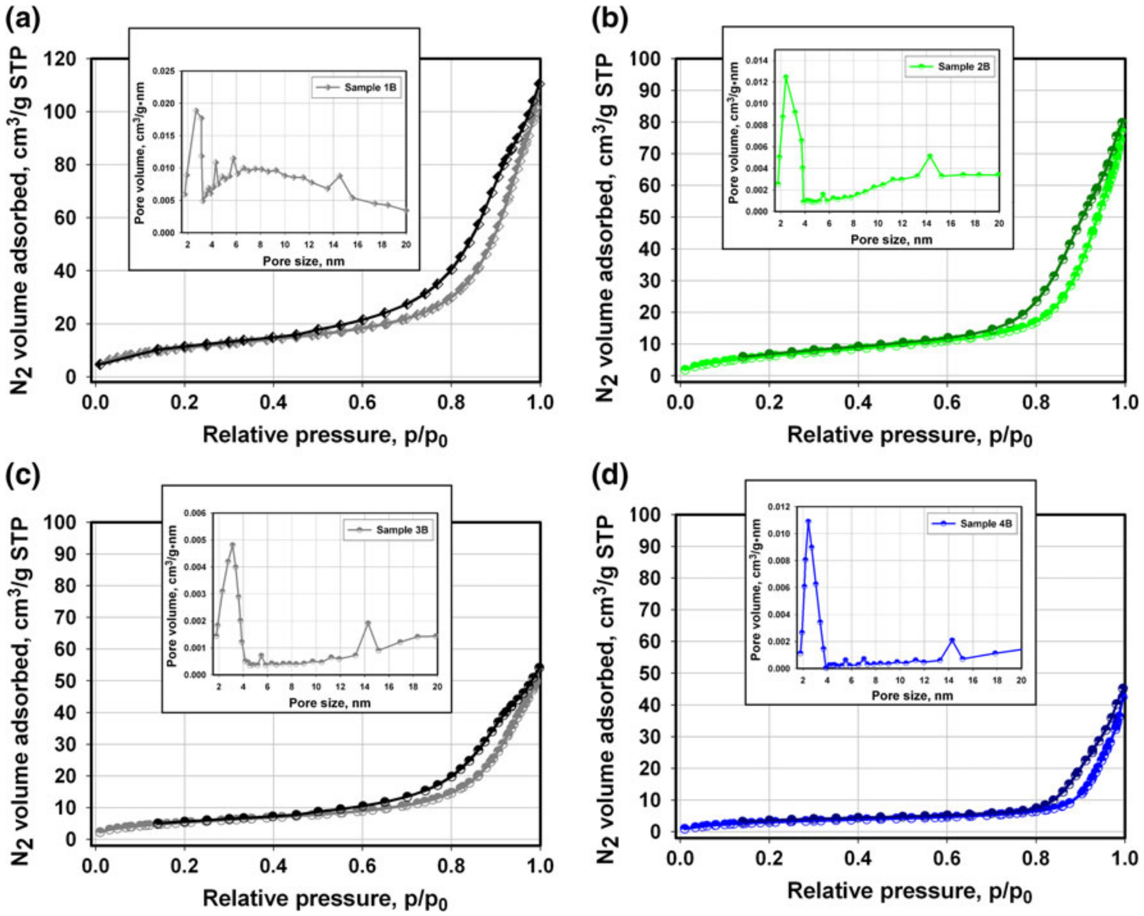

Fig. 7 Nitrogen adsorption/desorption isotherms and pore size distribution for unmodified emulsion silica (sample 1B (**a**)) and hybrids obtained using 3, 5 or 10 weight parts by mass of G-POSS (samples 2B (**b**), 3B (**c**), and 4B (**d**))

modified systems produced from it using 3, 5 or 10 weight parts by mass of G-POSS (Fig. 7), it was found that the character of the curves indicates that the analysed samples have a mesoporous structure. In the case of the pure silica (sample 1B), and the samples containing 3, 5 or 10 weight parts by mass of modifier (respectively samples 2B–4B), the volume of nitrogen adsorbed in the first stage was observed to show a gentle increase. When the relative pressure p/p_0 reached a value of approximately 0.6 there was a significant increase in the quantity of adsorbed nitrogen. For emulsion silica the quantity of nitrogen adsorbed at $p/p_0 = 1$ was 110 cm^3/g, while the quantities adsorbed for the hybrid systems produced with 3, 5 or 10 weight parts of G-POSS were respectively 80, 55, and 45 cm^3/g.

Based on analysis of the data given in Table 1, it was concluded that the BET specific surface area for emulsion silica (sample 1B) is 40 m^2/g. In turn the pore volume calculated using the method of BJH is 0.17 cm^3/g. As a result of functionalization of the surface of the silica support, a change in surface activity was observed. For example, for sample 4B a change in activity was recorded with a fall in the value of the specific surface area to 11 m^2/g (S_{BET}). Based on the obtained isotherms and corresponding algorithms, the pore volumes and diameters were determined. Pore diameters were found to increase from 16 to 24 nm, while the pore volume decreased—for the initial sample (1B) and the samples modified with 3, 5 or 10 weight parts

Table 2 Elemental content and degree of silica surface coverage with 3, 5 or 10 weight parts of G-POSS

Sample numbers	Elemental content (%)		Degree of coverage (μmol/m^2)
	C	H	
1A	0.139	1.124	–
2A	1.207	1.398	0.147
3A	2.442	1.577	0.308
4A	3.484	1.756	0.452
1B	2.398	1.112	–
2B	2.952	1.530	1.038
3B	3.676	1.749	1.318
4B	5.133	2.018	1.918

by mass of G-POSS, the respective values were 0.17, 0.12, 0.12 and 0.10 cm^3/g. In the course of the tests it was concluded that the changes in porous structure are evidence of the effectiveness of the modification process, which correlates with changes in the character of the surface of the samples.

At the next stage the chemical composition of the obtained materials was determined using elemental analysis (Table 2). This was performed in order to verify the effectiveness of the modification process, and to calculate the degree of coverage of the silica support surface with octakis({3-glycidoxypropyl}dimethylsiloxy) octasilsesquioxane. The degree of coverage was calculated from an equation based on the Berendsen and de Golan equation (1978).

As a result of functionalization of the silica supports with G-POSS, the content of carbon and hydrogen was found to increase with the applied quantity of modifier (in weight parts by mass). Because the degree of coverage depends on the specific surface area of the initial support, lower values were obtained for hydrated silica modified with POSS, respectively 0.147, 0.308, and 0.452 $\mu mol/m^2$ (Table 2). In the case of hybrid systems made from emulsion silica the computed values of the degree of coverage are 1.038, 1.318, and 1.918 $\mu mol/m^2$.

The morphology of the produced hybrid systems was also determined, using transmission electron microscope images (Fig. 8).

Significant changes were observed in the obtained morphological character of the materials. There was a change in particle size compared with the initial support. This is probably because of the hydrophilicity of the hydrated silica, for which significant agglomeration of particles was observed. As a result of the functionalization of silica with G-POSS, apart from the larger clusters of particles (secondary agglomerates), a significant proportion of primary particles was also observed.

An analogous tendency was recorded for the hybrid systems produced using emulsion silica and G-POSS in different quantities. The unmodified silica is characterized by spherically shaped particles. Modification using POSS with epoxide groups led to significant agglomeration of particles. For all functionalized systems (see Fig. 9b–d) a significant increase in grain size was observed, as can be seen on the TEM photographs (particularly in the case of sample 4B).

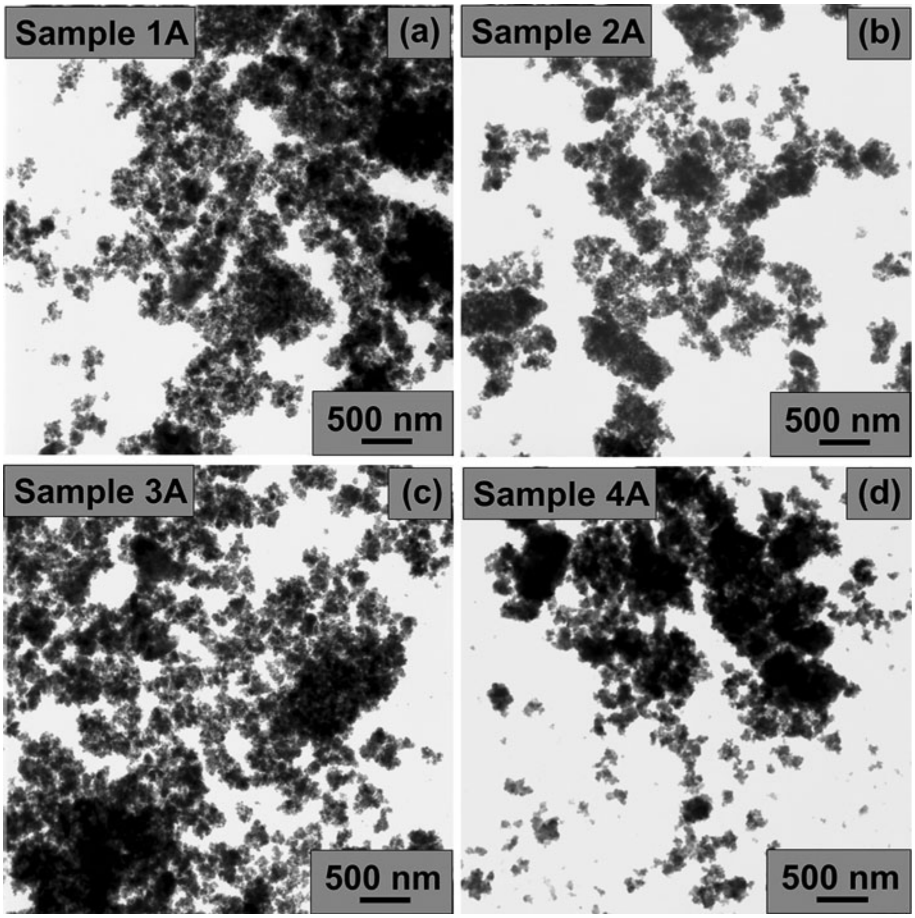

Fig. 8 TEM microphotographs of **a** pure hydrated silica, and hybrids obtained after modification of the silica with G-POSS in different quantities (**b**–**d**)

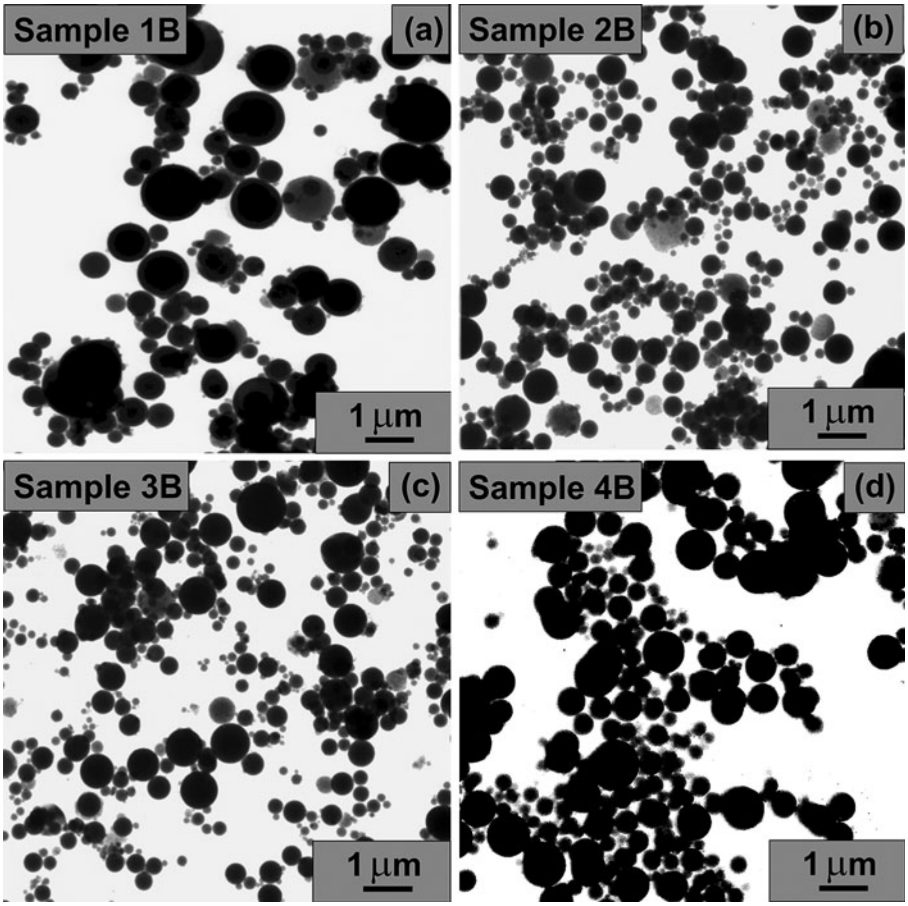

Fig. 9 Morphological characteristics (TEM images) of **a** pure emulsion silica, and the hybrid systems obtained after modification of the silica with G-POSS in different quantities (**b**–**d**)

The thermal stability of the pure silica fraction and of selected hybrids functionalized with octakis({3-glycidoxypropyl}dimethylsiloxy) octasilsesquioxane (G-POSS) was determined using thermal analysis. The tests were carried out in a nitrogen atmosphere, with the temperature varying from 30 to 1,000 °C, stepped at 10 °C/min. These tests produced the thermogravimetric curves shown in Fig. 10a, b.

Figure 10a shows TGA thermograms of the pure silsesquioxane used, the unmodified hydrated silica, and the hybrids obtained by functionalization of silica with 3, 5 or 10 weight parts by mass of G-POSS. For hydrated silica (sample 1A) the process of decomposition begins at a temperature of 30 °C, and it can be stated to be a one-stage process. The observed mass loss in the temperature range 30–125 °C is relatively rapid, as is indicated by the intense fall in mass recorded on the thermogravimetric curve. After the temperature exceeds 700 °C the sample stabilizes, and its mass remains almost unchanged. The analysis showed that within the aforementioned temperature range, pure hydrated silica loses only 10 % of its total mass.

The hybrid systems were analysed in order to determine their thermal stability, and the thermograms obtained were compared with the pure POSS modifier and with the initial silica support. For the hybrid systems (samples 2A–4A) a two-stage process of degradation was observed. The first mass loss, visible in a range from 30 to approximately 300 °C, is probably linked to the loss of chemically and physically bound water. In this range the mass loss is slightly above 7 %. The next inflection occurs when a temperature of approximately 320 °C is reached. This mass loss is probably associated with the decomposition of glycidoxypropyl functional groups. The mass of the systems stabilizes at a temperature of 700 °C, and the total loss of mass in the temperature range 30–1,000 °C for hybrid systems produced with 3, 5 or 10 weight parts by mass of POSS is between 8 and 15 %. No changes were observed in the improvement in the thermal stability of the systems as the quantity of modifier added was increased.

Figure 10b shows TGA curves for unmodified emulsion silica and for the hybrid systems produced from it. For all of the hybrid systems a two-stage decomposition process was recorded. The first drop on the thermogravimetric curve is associated with water dehydration (~300 °C), while the second mass loss, analogously as in the case of hybrids made from support precipitated from aqueous solutions, is associated with the degradation of organic substituents present in the corners of the POSS cage.

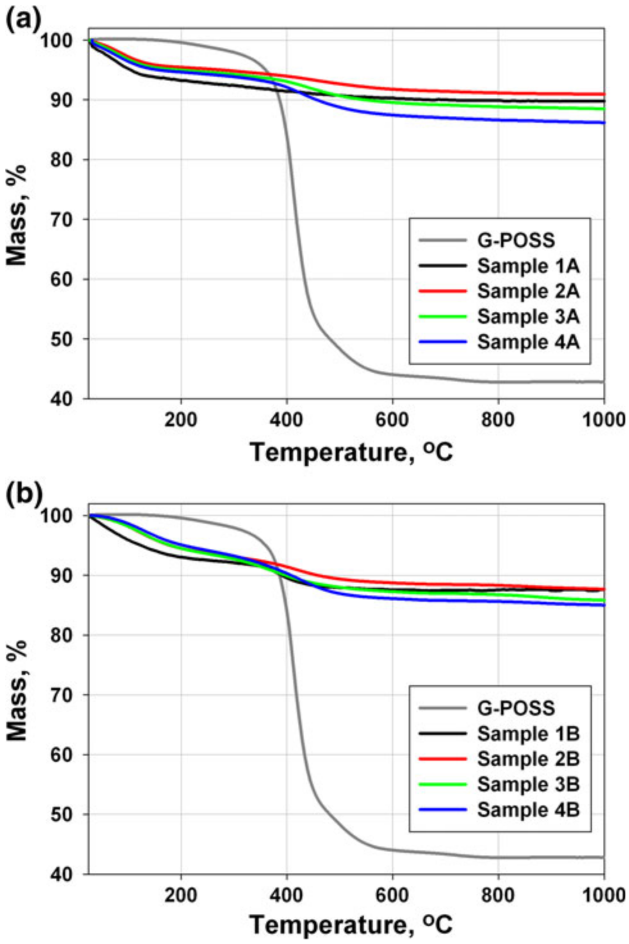

Fig. 10 Thermograms of pure G-POSS, **a** unmodified hydrated silica, **b** unmodified emulsion silica, both modified with 3, 5 or 10 weight parts by mass of G-POSS

The TGA curve for pure octakis({3-glycidoxypropyl}dimethylsiloxy) octasilsesquioxane (Fig. 10a, b) showed a mass loss of about 55 % at 400 °C. The process continued up to total degradation of the organic groups substituted at the silicon atoms of the POSS skeleton. The use of silica systems as supports for hybrid preparation caused a significant decrease in the total mass loss and thermal stability shift, which is very important with regard to the use of such systems in polymer processing and in other useful materials.

4 Conclusions

The proposed method of immobilization of octakis ({3-glycidoxypropyl}dimethylsiloxy) octasilsesquioxane on the surface of precipitated silica supports makes it possible to obtain modern products using the principle of chemical adsorption.

Epoxides are used because of their high reactivity, which is associated with the relative ease of opening of the strongly coupled three-member ring.

The chemistry of the functionalization reaction was investigated using the techniques of FTIR and ^{29}Si and ^{13}C CP MAS NMR. Moreover the effectiveness of the immobilization of G-POSS on the surface of the silica supports was verified by tests of adsorption activity. It was concluded that the character of the obtained curves indicates a mesoporous structure for both samples. It was also observed that the process of functionalization of the surface using POSS with epoxide groups led to an increase in pore diameters, while the pore volume decreased. This effect results from the blocking of active sites on the SiO_2 surface by molecules of the modifier.

When the surface of silica fillers is functionalized with POSS compounds, the degree of coverage increases with the quantity of applied modifier.

Changes in the thermal stability of the SiO_2/POSS hybrid systems were also determined, compared with pure cage silsesquioxane and the unmodified silica supports.

The hybrid systems obtained during the research are innovative materials which may be used, among other applications, as heterogeneous catalysts or as fillers with specific properties, containing reactive organic groups, which enable high physical adsorption or chemisorption into the polymer.

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