

Received March 21, 2012; reviewed; accepted April 23, 2012

## SYNTHESIS OF HEPTA(ISOBUTHYL)ETHYLTRIETHOXYSILYL-OCTASILSESQUIOXANE AND ITS APPLICATION AS A MODIFIER OF BOTH HYDRATED AND EMULSION SILICAS

Karolina SZWARC-RZEPKA\*, Filip CIESIELCZYK\*, Monika ZAWISZA\*, Michał KACZMAREK\*, Michał DUTKIEWICZ\*\*, Bogdan MARCINIEC\*\*, Hieronim MACIEJEWSKI\*\*\*, Teofil JESIONOWSKI\*

\* Poznan University of Technology, Faculty of Chemical Technology, Institute of Chemical Technology and Engineering, M. Skłodowskiej-Curie 2, PL-60965, Poznan, Poland, E-mail: Teofil.Jesionowski@put.poznan.pl, phone: +48(61)6653720, fax: +48(61)6653649

\*\* Adam Mickiewicz University, Faculty of Chemistry, Department of Organometallic Chemistry, PL-60780, Grunwaldzka 6, Poznan, Poland

\*\*\* Poznan Science and Technology Park, Rubież 46, PL-61612 Poznan, Poland

**Abstract.** Hepta(isobutyl)ethyltriethoxysilyloctasilsesquioxane was synthesized by hydro-silylation of hepta(isobutyl)vinyloctasilsesquioxane with triethoxysilane, over Karstedt catalyst and tetrahydrofuran. Hybrid systems of silica and monofunctional silsesquioxane ( $\text{SiO}_2/\text{POSS}$ ) were obtained by solvent evaporation, using emulsion silica (ES) and hydrated silica (HS), obtained by precipitation in emulsion or water media. For their surface modification hepta(isobutyl)ethyltriethoxysilyloctasilsesquioxane was used. The hybrids were characterized by dispersion analysis (NIBS method and laser diffraction technique) and morphological analysis (transmission electron microscopy) as well as wettability profiles in an aqueous system. The adsorptive properties of the hybrids were evaluated on the basis of surface area BET, pore volume and size. The effectiveness of modification of the hybrid fillers was tested by FTIR and  $^{29}\text{Si}$  CP MAS NMR.

**keywords:** *silica, surface modification, silsesquioxanes cage, hybrid nanofillers*

### 1. Introduction

Polyhedral Oligomeric Silsesquioxanes or POSS make an important group of organic-inorganic hybrid materials. They occur in many varieties differing in the size of cages, the number and type of side groups (Iyer, 2007). Particularly stable is  $T_8$  silsesquioxane in which the organic groups R are attached to the inorganic fragments of each vertex of a silsesquioxane cage containing Si–O–Si group (Wallace, 2000).

The chemistry of silsesquioxanes is dominated by the chemistry of  $T_8$  and its derivatives, which is related to its easy synthesis, easy isolation from the reaction mixture and high yields of the processes in which it is involved when compared to those of the other POSS (Janowski, 2008). POSS show many interesting properties

such as thermal stability, easy chemical modification and tendency to formation of nanometric size particles (Madhavan, 2009).

POSS containing 8 silicon atoms in its molecule ( $T_8$ ) is most often used in synthesis of polymers (Tang, 2009; Lin, 2009), in dentistry (Wu, 2009), microelectronics and optics (Matisons, 2010). Silicas modified with cage POSS have been so far used only for determination of catalytic properties of metallocenes (Bianchini, 2005).

The main aim of this work was the synthesis of hepta(isobutyl)-ethyltriethoxysilyloctasilsesquioxane and its application as a modifier of hydrated and emulsion silicas. Moreover, the influence of such modification process on the physicochemical properties of hybrid fillers obtained was evaluated.

## 2. Experimental

### 2.1. Synthesis of hepta(isobutyl)ethyltriethoxysilyloctasilsesquioxane

Hepta(isobutyl)ethyltriethoxysilyloctasilsesquioxane (K-POSS) was synthesized in the hydrosilylation reaction of previously synthesized hepta(isobutyl)-vinyloctasilsesquioxane (Żak, 2009) with triethoxysilane (Fig. 1). The process was carried out in the presence of a Karstedt catalyst and THF as a solvent. Hepta(isobutyl)vinyloctasilsesquioxane (5 g, 5.9 mmol), triethoxysilane with 10% excess (1.1 g, 6.7 mmol) together with 100 cm<sup>3</sup> of THF as a solvent were placed in a three necked, round bottom flask equipped with a thermometer, condenser and magnetic bar. The Karstedt catalyst (3.7 mg, 4.07·10<sup>-7</sup> mol Pt) was added at room temperature and the solution was heated to 60°C and kept at this temperature overnight. Then, the solvent and the excess of triethoxysilane were evaporated under vacuum to give the product as white powder (5.8 g, 98% of theoretical yield).

To control the course of synthesis and to verify the products structure the spectra: <sup>1</sup>H NMR (300 MHz), <sup>13</sup>C NMR (75 MHz) and <sup>29</sup>Si NNR (59 MHz) were recorded on a Varian XL 300 spectrometer at room temperature using C<sub>6</sub>D<sub>6</sub> as solvent. All chemicals were used as received from suppliers without any further purification.

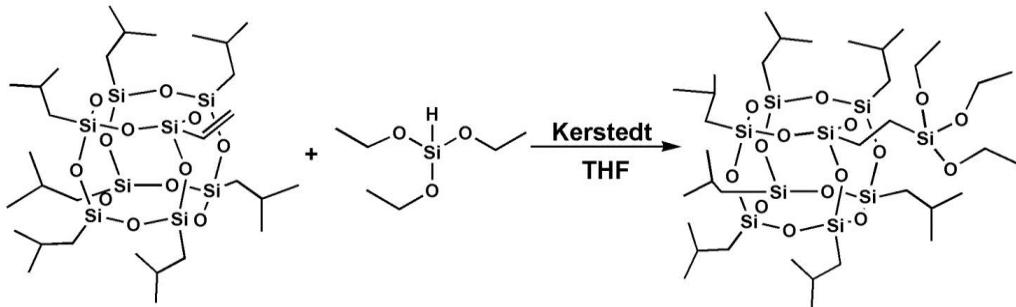


Fig. 1. Synthesis of hepta(isobutyl)ethyltriethoxysilyloctasilsesquioxane (K-POSS)

## 2.2. $\text{SiO}_2/\text{POSS}$ hybryd synthesis

The process was begun with production of silicas on a large laboratory scale. Two types of silica were prepared, obtained in the emulsion (ES) or in the aqueous (HS) system. The idea of production of silica fillers was presented in detail by Jesionowski (2003, 2009). The  $\text{SiO}_2/\text{POSS}$  hybrids were obtained by solvent evaporation. At first a fraction of ES or HS silica was introduced into the reactor and then on the silica surface a mixture made of a monosubstituted silsesquixane cage and 30 cm<sup>3</sup> 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 of  $\text{SiO}_2$ . After introduction of the whole portion of the mixture, the contents were moved into a flask of 500 cm<sup>3</sup> in capacity and placed in a vacuum evaporator Rotavapor RII made by Büchi Labortechnik AG to perform the modification and to evaporate the solvent. Finally the product was subjected to convection drying at 120°C for 48h (chamber drier SEL-I3, made by Memmert). The idea of synthesis of hybrid fillers is schematically presented in Fig. 2.

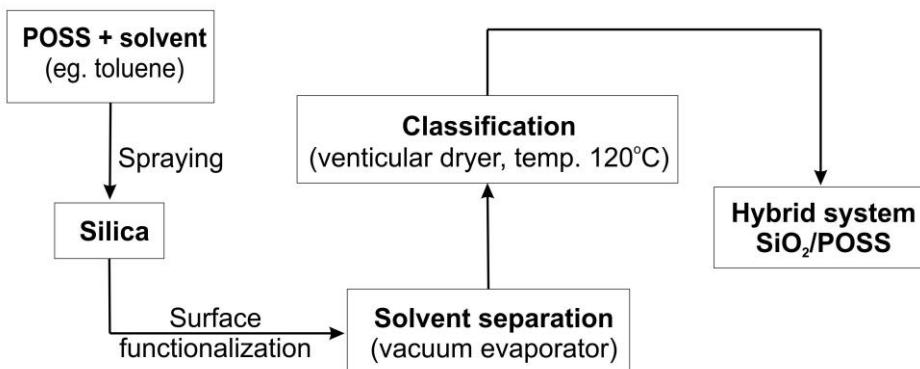


Fig. 2. A scheme of synthesis of  $\text{SiO}_2/\text{POSS}$  hybrids

The final product was characterized by a number of methods. 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 method) and 0.2–2000 µm (laser diffraction technique). Microstructure of the samples was analyzed by using the transmission electron microscopy images (Joel 1200 EX II). The wettability with water was measured by a tensiometer K100 made by Krüss equipped with necessary attachments. For selected hybrid systems the nitrogen adsorption/desorption isotherms were recorded using an ASAP 2020 analyzer, made by Micromeritics Instrument Co. On the basis of the isotherms the specific surface area BET ( $S_{\text{BET}}$ ) was calculated and the pore size ( $S_p$ ) and volume ( $V_p$ ) were found from BJH equation. The effectiveness and degree of

modification of  $\text{SiO}_2$  with POSS were estimated using the FTIR IFS 66v/S spectrophotometer made by Bruker. The  $^{29}\text{Si}$  CP MAS NMR spectra analysis of unmodified and modified silicas was conducted with a DSX spectrometer (Bruker).

### 3. Results and discussion

Results of NMR analysis of the silsesquioxane product confirmed its structure:  
 $^1\text{H}$  NMR ( $\text{C}_6\text{D}_6$ , 298K, 300 MHz) ppm: 0.78–0.92 ( $\text{CH}_2$ ), 1.02–1.09, 1.23–1.38 ( $\text{CH}_3$ ), 1.93–2.14 ( $\text{CH}$ ), 4.32–4.54 ( $-\text{OCH}_2$ ),  
 $^{13}\text{C}$  NMR ( $\text{C}_6\text{D}_6$ , 298K, 75.5 MHz) ppm: 6.3 ( $\text{CH}_2\text{Si}$ ), 13.4 ( $\text{SiCH}_2$ ), 18.8 ( $\text{CH}_3$ ), 22.5, ( $\text{CH}_2$ ), 23.9 ( $\text{CH}$ ), 26.2 ( $\text{CH}_3$ ), 53.3 ( $-\text{OCH}_2$ ),  
 $^{29}\text{Si}$  NMR ( $\text{C}_6\text{D}_6$ , 298K, 59.6 MHz) ppm: -64.6, -66.9, -67.7, -68.2.

Functionalization of silica was performed with monosubstituted hepta(isobutyl)ethyltriethoxysilyloctasilsesquioxane (K-POSS). Table 1 presents the data characterizing dispersive and physicochemical properties of the hybrids obtained.

Table 1. Dispersion characterization and physicochemical properties of the hybrid systems made of hydrated silica (HS) and hepta(isobutyl)ethyltriethoxysilyloctasilsesquioxane

Sample No.	Amount of POSS modifiers (wt./wt.)	Polydispersity index (PdI)	Diameters from Zetasizer Nano ZS (nm)	Diameters from Mastersizer 2000 ( $\mu\text{m}$ )			
				d(0.1)	d(0.5)	d(0.9)	D[4.3]
1	—	0.514	91–220 3090–6440	5.91	15.40	30.64	17.18
2	3	0.663	122–342	5.84	28.68	83.06	66.00
3	5	0.543	122–342	5.72	28.48	91.58	76.00
4	10	0.749	91–220 1110–3580	6.03	31.93	96.57	79.00

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

Analysis of Table 1 data for the hybrid made with HS has revealed that sample 3, obtained with 5 weight parts by mass of K-POSS shows the lowest degree of agglomeration. Moreover, the polydispersity index for this sample is 0.543. The particle size distribution measured for sample 3 shows only one band covering the particle diameters from the range 122–342 nm. The same range of particle diameters was also found for sample 2, although the maximum volume contributions of particles were different for these two samples. The greatest tendency towards agglomeration was noted for sample 4, which is related to the use of the greatest amount of the modifier for its preparation.

The sizes of particles in samples 2–4, measured by Mastersizer 2000 (Table 1), varied in practically the same ranges of diameters. In sample 3 obtained with 5 weight

parts by mass of K-POSS (sample 3) 10% of particles had diameters not greater than 5.72 µm and 50% of particles had diameters not greater than 28.48 µm and 90% not greater than 91.58 µm. The mean diameter of particles in this sample D[4.3] corresponded to agglomerations of the maximum diameter of 76.00 µm. TEM images of samples 2, 3 and 4 obtained with 3, 5 and 10 weight parts by mass of K-POSS (Fig. 3) 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 2 and 3, (Figs. 3b, c). Despite the worse dispersion parameters, sample 4 (Fig. 3d) has particles of the greatest refinement, they are much smaller and the clusters they make are also small.

The hybrid systems obtained by functionalization of emulsion silica (ES) with K-POSS show much different dispersive and morphological character. The relevant data are presented in Table 2. As follows from these data, sample 7 (ES grafted with 5 weight parts by mass K-POSS) is characterised 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 0.219. Sample 7 also shows the lowest tendency towards agglomeration (Fig. 4b). Its particles have spherical shape and their adhesion to irregular K-POSS particles is rather strong.

Samples 6 and 8 obtained with 3 and 10 weight parts by mass of K-POSS have definitely inhomogeneous character, their particles are greater and their polydispersity indices are higher. The differences in dispersion characteristics are illustrated by TEM images (Fig. 4b,d). These samples have spherical shape particles, making primary and secondary agglomerations. Because of significant hydrophobicity of these samples, no measurements of particle size distribution by the laser diffraction method were made. The SiO<sub>2</sub>/POSS hybrid systems obtained by mechanical method were characterized by much different dispersive and morphological properties (Szwarc 2012). The final products obtained by the mechanical method with the use of mortar mill, were made of particles with diameters of the order of 200 nm, despite the use of micrometric hydrated silica as the matrix for functionalization.

Table 2. Dispersion and physicochemical characterization of hybrid systems made of emulsion silica and hepta(isobutyl)ethyltriethoxysilyloctasilsesquioxane (K-POSS)

Sample No.	Amount of POSS modifiers (wt./wt.)	Polydispersity index (PdI)	Diameters from Zetasizer Nano ZS (nm)
5	—	0.252	255–712
6	3	0.268	531–1480
7	5	0.219	255–1280
8	10	0.447	825–2300

At the next step of hybrids characterization they were subjected to a water wettability analysis. Figure 5 presents the wettability profiles of the initial hydrated

silica and the hybrids based on HS obtained with the use of 3, 5 and 10 weight parts by mass of K-POSS (samples 1–4), while Fig. 6 shows the wettability profiles of ES and the hybrids made of ES and K-POSS (samples 5–8). The greatest tendency to water absorption was found for sample 1, while the lowest amount of water was absorbed by sample 4, modified with 10 wt./wt. of K-POSS. The character of the wettability profiles indicates that with increasing amount of the modifying monofunctional POSS, the hydrophobic character of the product increases

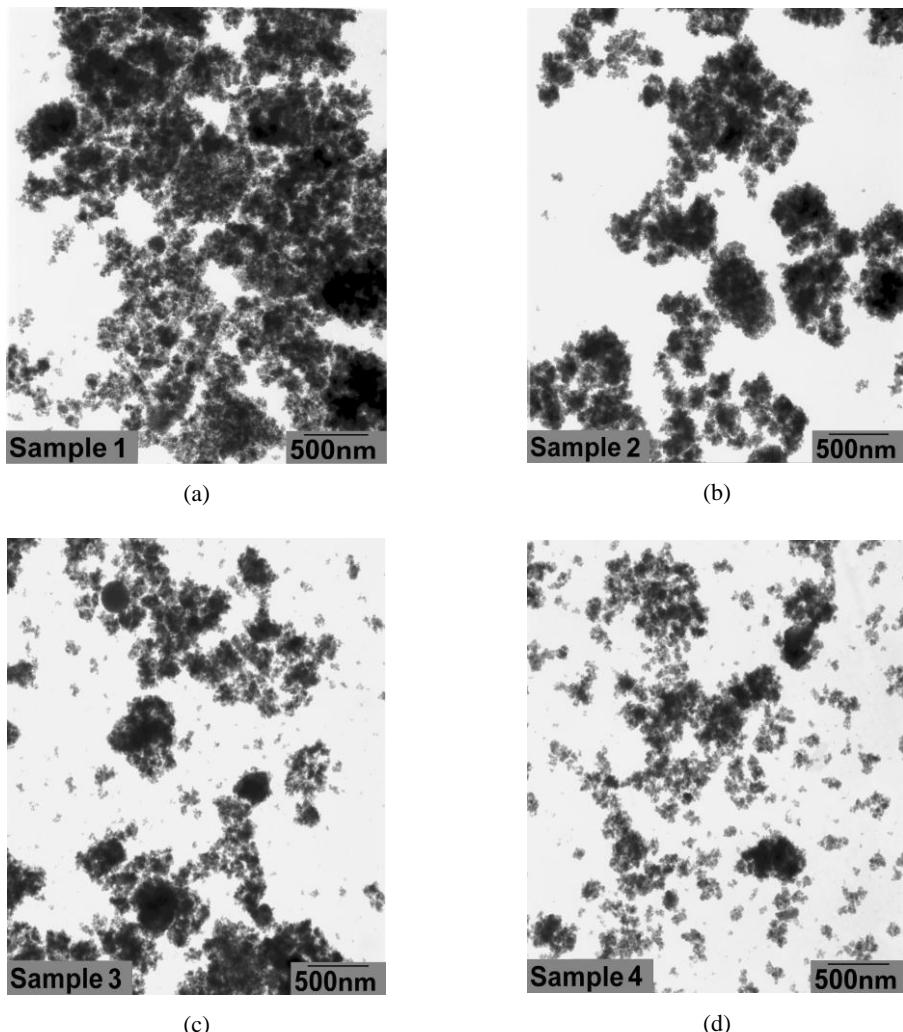


Fig. 3. TEM microphotographs of (a) pure hydrated silica and hybrid modified with (b) 3, (b) 5, and (d) 10 weight parts by mass of hepta(isobutyl)ethyltriethoxysilyloctasilsesquioxane (K-POSS)

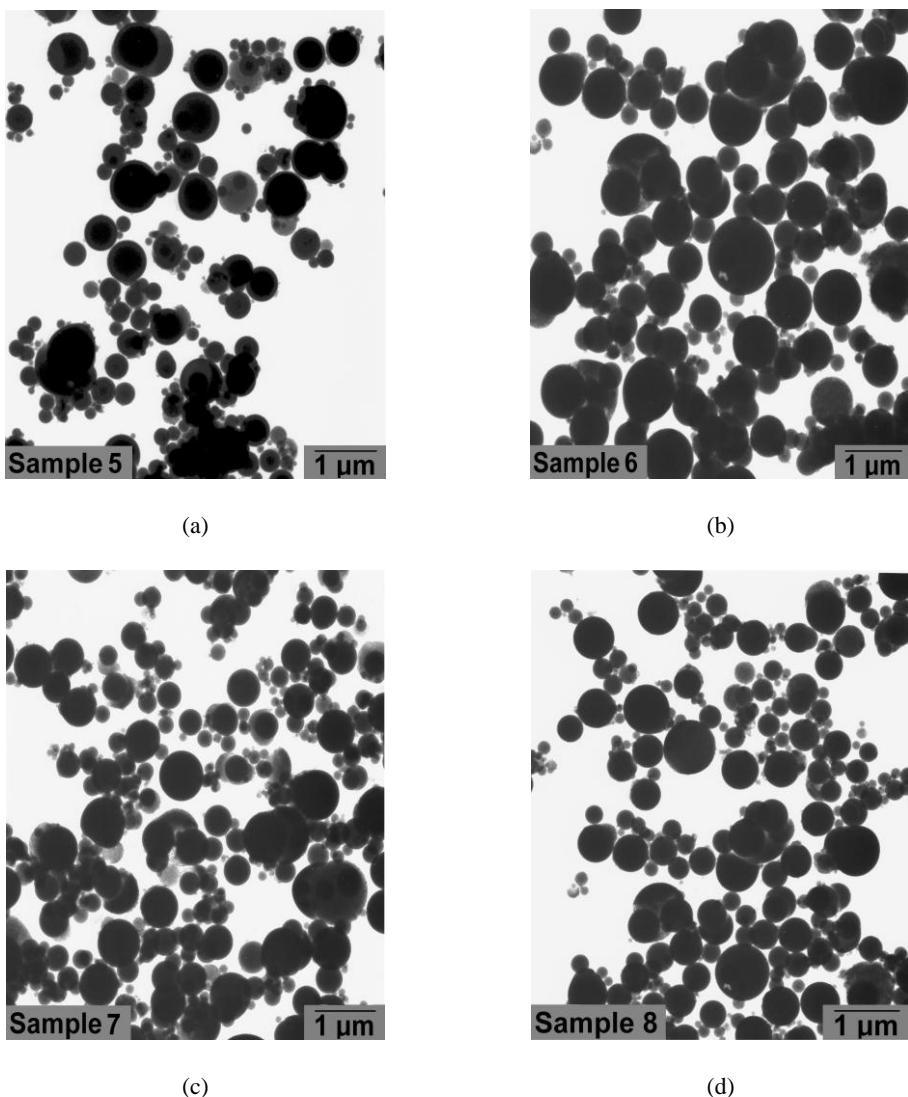


Fig. 4. TEM microphotographs of (a) pure emulsion silica and hybrid modified with (b) 3, (b) 5, and (d) 10 weight parts by mass of hepta(isobutyl)ethyltriethoxysilyloctasilsesquioxane (K-POSS)

The hybrids with K-POSS based on silica precipitated from the emulsion system show similar tendencies to water absorption, although sample 5 has the highest sorption capacity expressed by a mass increase of 0.32 g. The smallest mass increase was noted for sample 8, obtained with the use of 10 wt./wt. of K-POSS. It should be emphasised that the initial silicas differed significantly in hydrophilic character. Hydrated silica absorbed about 50% more water than emulsion silica.

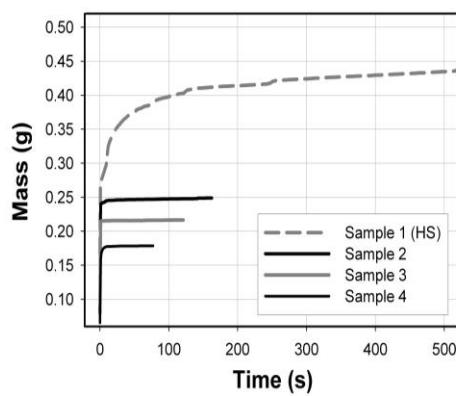


Fig. 5. Wettability profiles obtained for hydrated silica (HS) and selected  $\text{SiO}_2/\text{POSS}$  hybrids

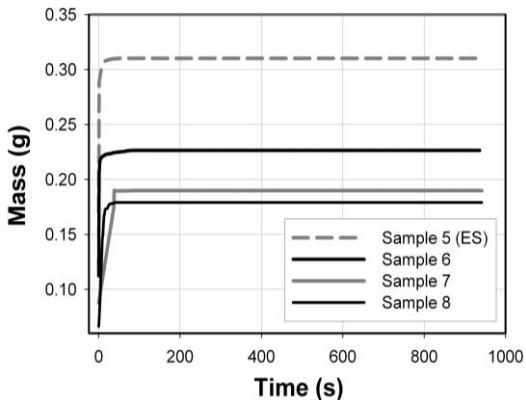
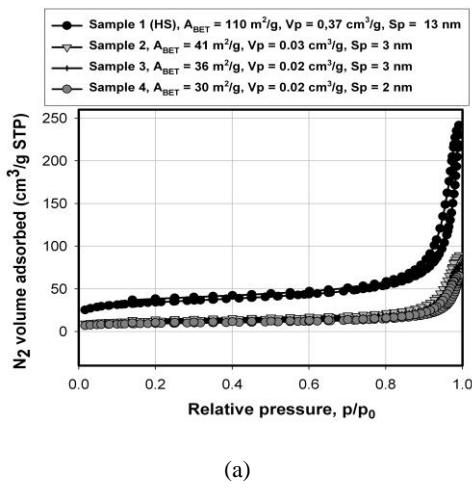
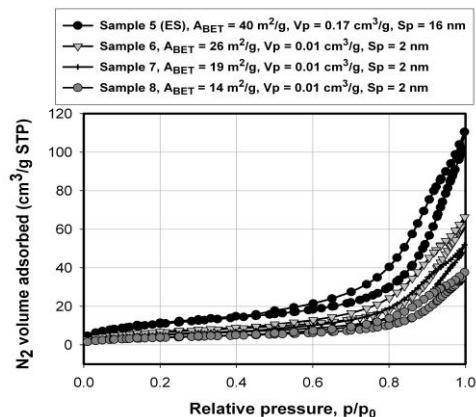


Fig. 6. Wettability profiles obtained for emulsion silica (ES) and selected  $\text{SiO}_2/\text{POSS}$  hybrids



(a)



(b)

Fig. 7. Nitrogen adsorption/desorption isotherms and adsorptive properties for: (a) unmodified HS (sample 1), (b) unmodified ES (sample 5) and silicas modified with 3, 5 or 10 weight parts by mass of hepta(isobutyl)ethyltriethoxysilyloctasilsesquioxane (K-POSS)

To evaluate the adsorptive properties of the samples studied, they were subjected to determination of nitrogen adsorption/desorption isotherms. Analysis of the isotherms permitted determination of the surface area as well as pore volume and diameters (see Fig. 7). Figure 7 presents the nitrogen adsorption/desorption isotherms for the unmodified hydrated silica (HS) and emulsion silica (ES) samples and for the hybrids modified with 3, 5 or 10 wt./wt. of K-POSS. The isotherms show a systematic increase in the volume of adsorbed nitrogen with increasing relative pressure till reaching a maximum value of  $240 \text{ cm}^3/\text{g}$  for sample 1 at  $p/p_0=1$  (Fig. 7a). For hybrids the

increase in the volume of adsorbed nitrogen after the threshold value ( $p/p_0 = 0.7$ ) is not so steep and the maximum values for  $p/p_0 = 1$  are much lower. Also the specific surface area, pore volume and pore size were drastically lower than those for unmodified samples, e.g.  $A_{\text{BET}} = 30 \text{ m}^2/\text{g}$  for sample 4 modified with 10 wt./wt. of K-POSS. A similar effect is observed for the hybrids based on ES; for the unmodified silica the specific surface area ( $A_{\text{BET}}$ ) was  $40 \text{ m}^2/\text{g}$  and for sample 8 it has decreased to  $14 \text{ m}^2/\text{g}$  (Fig. 7b). These changes are consequences of blocking the active centres on the  $\text{SiO}_2$  surface by the molecules of silsesquioxane. The pore size determined proves the mesoporous character of the hybrids obtained.

Figure 8 presents the FT-IR spectra of the unmodified silicas (HS and ES) and the hybrids obtained after the silicas modifications with 10 wt./wt. of K-POSS.

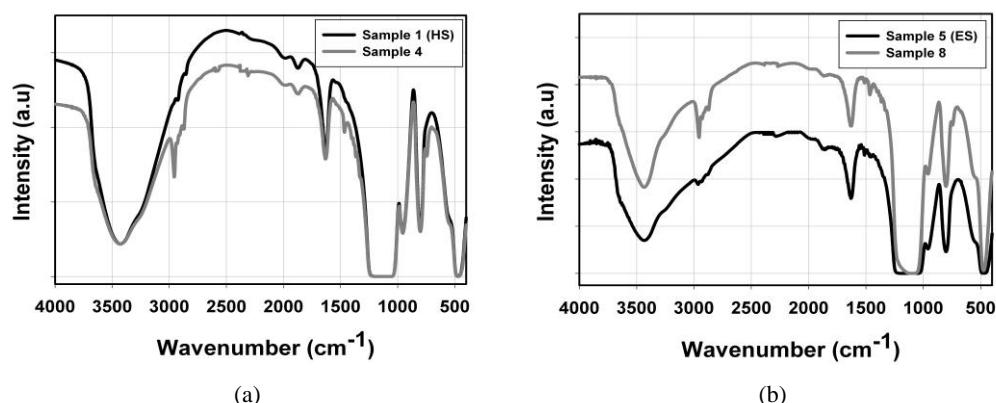


Fig. 8. FT-IR spectra of unmodified silicas (samples 1 and 5) and the hybrids obtained by their modification with 10 wt./wt. of K-POSS (samples 4 and 8)

The FT-IR spectra (Fig. 8) revealed signals typical of K-POSS used for silica surface modification. In the range  $3700\text{--}3200 \text{ cm}^{-1}$  the spectra show the signals corresponding to the stretching vibrations of hydroxyl groups from the adsorbed water molecules. In each spectrum there was a signal assigned to  $\delta(\text{C-H})$  in the range  $2900\text{--}2850 \text{ cm}^{-1}$ . At  $1350 \text{ cm}^{-1}$  there is a band assigned to the bending vibrations of  $\gamma(\text{C-H})$  groups. The bands appearing in the range  $1500\text{--}1450 \text{ cm}^{-1}$  and  $860\text{--}700 \text{ cm}^{-1}$  are characteristic of the vibrations of Si-C bond. Strong bands at  $1100 \text{ cm}^{-1}$  and  $500 \text{ cm}^{-1}$  correspond to the stretching vibrations of Si-O-Si. At about  $850 \text{ cm}^{-1}$  there is a band assigned to  $\delta(\text{C-C})$  from isobutyl groups of K-POSS. Comparing the spectra presented in Fig. 8a and 8b, no significant differences were found in the content of characteristic functional groups in the filler structure, irrespective of the type of silica used.

The effectiveness of silica modification with K-POSS was verified by the  $^{29}\text{Si}$  CP MAS NMR spectra, which are presented in Figs. 9 and 10.

The  $^{29}\text{Si}$  CP MAS NMR spectrum of unmodified HS (Fig. 9) shows two signals at  $-110$  and  $-100 \text{ ppm}$ . The main signal at  $-110 \text{ ppm}$  is assigned to three siloxane groups

and one silanol group ( $Q^3$ ), while the signal at  $-100$  ppm corresponds to four siloxane bridges ( $Q^4$ ,  $\equiv\text{Si}-\text{O}-\text{Si}\equiv$ ). The spectra of samples modified with K-POSS besides the  $Q^3$  and  $Q^4$  signals also have a band assigned to  $T^3$  group at  $-67$  ppm. Although the presence of  $T^2$  and  $T^3$  structures testifies to the chemical modification of  $\text{SiO}_2$  surface, we cannot draw such conclusions as no changes in the intensities of  $Q^3$  and  $Q^4$  signals were observed as a result of functionalization with K-POSS.

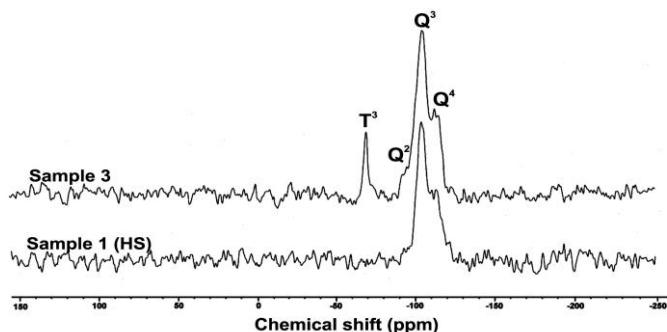


Fig. 9.  $^{29}\text{Si}$  CP MAS NMR spectra of unmodified HS (Sample 1) and silica functionalized with 5 wt./wt. K-POSS (Sample 3)

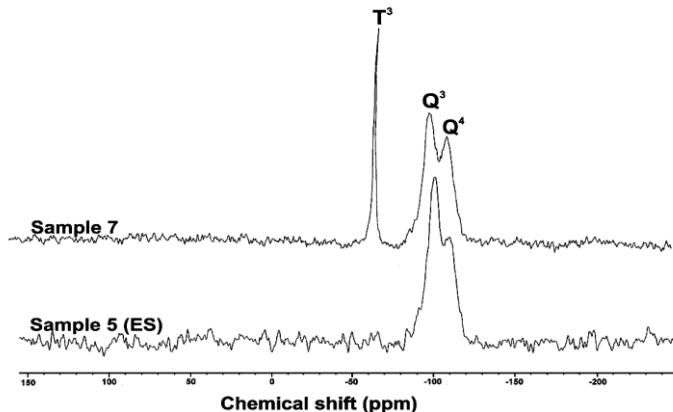


Fig. 10.  $^{29}\text{Si}$  CP MAS NMR spectra of unmodified ES (sample 5) and silica functionalized with 5 wt./wt. of K-POSS (sample 7)

The spectrum of unmodified ES (sample 5) reveals three characteristic signals at  $-110$ ,  $-100$  and  $-99$  ppm. The latter small signal is assigned to the double silanol groups, to the so-called silicon site  $Q^2$ . The spectrum of sample 7 shows additionally the  $T^3$  structure ( $-67$  ppm), characteristic of condensation of the modifier (K-POSS) with the silica support. As a result of silica functionalization, a change in the intensity

of signals corresponding to the silanol ( $\text{Q}^3$  –100 ppm) and siloxane ( $\text{Q}^4$ , –110 ppm) groups, which could indicate that chemical adsorption have taken place. However, because of the lack of  $\text{T}^2$  structure, we can conclude only about the adhesion of cage POSS to the silica surface.

Recently, the interest in the hybrid systems has been increasing. A combination of inorganic matrix with organic-inorganic cage POSS gave products showing a number of interesting physicochemical and dispersive-morphological properties.

Modification of silica supports gives changes in the dispersive and morphological properties and enhances the hydrophobic character of the products. The process of silica modification with K-POSS proved effective as evidenced by the results of FTIR, NMR analysis and adsorption parameters. Functionalization of silica with selected POSS compounds permits controlling of the physicochemical properties of the products to meet specific target demands.

#### **4. Conclusions**

The proposed method of silica modification involving solvent evaporation has brought products of homogeneity lower than that of the initial silicas. Functionalization of the silica surface with hepta(isobutyl)ethyltriethoxy silyloctasilsesquioxane (K-POSS) gave products containing greater size particles, showing a tendency to formation of primary and secondary agglomerates. Much better dispersive properties were obtained for the products based on the amorphous hydrated silica.

With increasing amount of the monosubstituted POSS used for functionalization, the products obtained showed increasingly higher hydrophobic character.

The functionalization with K-POSS also resulted in a significant reduction of the surface area BET, e.g. from 110 m<sup>2</sup>/g for the unmodified hydrated silica to 30 m<sup>2</sup>/g for the hybrid filler (sample 4). The same tendency was noted for the emulsion silica. The other parameters characterizing adsorptive properties such as the pore diameters and pore volume as well as the amount of nitrogen adsorbed, were also much decreased.

The proposed method of silica modification with K-POSS had advantageous effect on the physicochemical parameters as evidenced by the FT-IR results.

Analysis of <sup>29</sup>Si CP MAS NMR spectra confirmed no chemical interactions between the silica support and the K-POSS modifier. The results indicated the condensation phenomenon and strong adhesion of the modifier to the support.

#### **Acknowledgement**

The study was realized within the Development Project POIG 01.03.01-30-173/09 Nanosil from the European Fund of Regional Development within the operation programme Innovative Economy.

#### **References**

- BIANCHINI D., GALLAND G.B., DOS SANTOS J.H.Z., WILLIAMS R.J.J., FASCE D.P., DELL'ERBA I.E., QUIJADA R., PEREZ M., 2005, *Metallocene supported on a Polyhedral*

- Oligomeric Silsesquioxane-modified silica with high catalytic activity for ethylene polymerization*, Journal of Polymer Science: Part A: Polymer Chemistry, 43, 5465–5476.
- IYER S., ABU-ALI A., DETWILER A., SEHIRALDI A., 2007, *Transparent polymer – Polyhedral Oligomeric Silsesquioxane composites*, ACS Symposium Series (Science and Technology of Silicones and Silicone-Modified Materials), Cleveland, 964, 313–325.
- JANOWSKI B., PIELICHOWSKI K., 2008, *Polimery nanohybrydowe zawierające polidryczne oligosilseskioksany*, Polimery, 53, 87–98.
- JESIONOWSKI T., 2009, *Preparation of spherical silica in emulsion systems using the co-precipitation technique*, Materials Chemistry and Physics, 113, 839–849
- JESIONOWSKI T., ŻURAWSKA J., KRYSZTAKIEWICZ A., POKORA M., WASZAK D., TYTUS W., 2003, *Physicochemical and morphological properties of hydrated silicas precipitated following alkoxy silane surface modification*, Applied Surface Science 205, 212–224.
- LIN P., KHARE R., 2009, *Molecular simulation of cross-linked epoxy and epoxy-POSS nanocomposite*, Macromolecules, 42, 4319–4327.
- MADHAVAN K., GNANASEKARAN D., REDDY B.S.R., 2009, *Synthesis and characterization of poly(dimethylsiloxane-urethane) nanocomposites: Effect of (in)completely condensed silsesquioxanes on thermal, morphological, and mechanical properties*, Journal of Applied Polymer Science, 114, 3659–3667.
- MATISONS J., 2010, *Applications of Polyhedral Oligomeric Silsesquioxanes*, Springer, New York.
- SZWARC K., SIWINSKA-STEFANSKA K., MARCINIEC B., JESIONOWSKI T., 2012, *Synthesis and characterisation of SiO<sub>2</sub>/POSS hybrid systems obtained using the mechanical method*, Physicochemical Problems of Mineral Processing, 48, 181–192.
- TANG Y., LEWIN M., 2009, *Migration and surface modification In polypropylene (PP)/polyhedral oligomeric silsequioxane (POSS) nanocomposites*, Polymers Advanced Technologies, 20, 1–15.
- WALLACE W.E., GUTTMAN C.M., ANTONUCCI J.M., 2000, *Polymeric silsesquioxanes: degree-of-intramolecular-condensation measured by mass spectrometry*, Polymer 41, 2219–2226.
- WU J., MATHER P.T., 2009, *POSS Polymers: Physical properties and biomaterials applications*, Journal of Macromolecular Science, Part C: Polymer Reviews, 49, 25–63.
- ŻAK P., PIETRASZUK C., MARCINIEC B., SPÓLNIK G., DANIKIEWICZ W., 2009, *Efficient functionalisation of cubic monovinylsilsesquioxanes via cross-metathesis and silylative coupling with olefins in the presence of ruthenium complexes*, Advanced Synthesis and Catalysis, 351, 2675–2682.